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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

WILLIAM CROOKES, F.R.S., &c.

VOLUME LIX.—1889.

LONDON:
PUBLISHED AT THE OFFICE, BOY COURT, LUDGATE HILL, E.C.
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THE CHEMICAL NEWS.

VOLUME LIX.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1519.—JANUARY 4, 1889.

ON SOME NEW FOSSIL RESINS FROM THE COAL MEASURES.*

By W. IVISON MACADAM, F.R.S.E.,
Professor of Chemistry, New Veterinary College, Edinburgh.

My attention was directed some time ago by Mr. R. Kidston, F.G.S., to certain brown scales found in some coals. On treating these scales with solvents I found them to be of a resinoid nature. Mr. Kidston was of opinion that the substances might have been secreted by the carboniferous Lycopods (*Lepidodendros sigillari*), as it is now pretty well proved that the two lateral cicatricules of the vascular scar of the leaf are secretary glands, only the central cicatricule being that of the vascular bundle. There is another source, however, from which the resin might have been derived, viz., macrospore, which so largely enter into the composition of some coals. At present, so far as our observations go, the source of the resins cannot be definitely determined, but it appears most probable that they have been derived from one of the two, or both the sources suggested.

The coals experimented on were obtained from the neighbourhood of Kilmarnock and Methil. In these two districts the resins are found in layers in the coals, and can be readily detected by the eye. In the Methil district the resins are found in largest quantity in the "Chemise" coal. This seam, although not the thickest in the coal measures of Fife, is probably the finest and most valuable seam in the series. Its maximum thickness is about ten feet; the lower portion being rough or steam coal, the upper part splint and household coal. The resins are most largely found in the upper portion. We are, however, aware that resins are distributed throughout the whole of the coal measures, and I have already isolated many of these substances, and am now proceeding with the analyses.

In this communication I only deal with four resins; two of which were derived from the Kilmarnock coal and two from the Chemise seam.

In our first experiments the solvent employed was chloroform, but after tests showed that the material so obtained was *partially* soluble in ether. In our latter work we have first extracted with ether and then treated the residue with chloroform. In this manner the resinoid substances are divided into two distinct portions. We have not yet determined whether the ether resin or the chloroform-soluble resin can be further sub-divided, but we propose to determine this point. The ether soluble resins are, not only in the substances now specially treated, but in materials derived from other coals, partially volatile at temperatures much below 100° C., and we argue from this fact either that the bodies are complex, or that they are broken up at comparatively low temperatures. We specially mention this fact, as it has a direct bearing on an informal communication made by Professor Bedson to the Society of Chemical Industry at a meeting of the Newcastle Section, held in the Durham College of Science on November 8 this year, and reported in the *Journal* of the Society for that month (p. 729). In that communication Professor Bedson, referring to certain gases occluded by coal, states that he has obtained such by placing the coals "in suitable vessels and exhausting them by a Sprengel pump, and at the same time heating the coal at 100° C. (212° F.), drawing off the released gases by the continual flow of mercury." We would point out that many, if not all, coals, when heated to these temperatures, have a portion of their resins either volatilised or broken up, and we have found that the pure resins, when heated, do give off gases of the CH_4 and C_2H_4 series. We are also aware that the composition of coal dust has much to do with its explosive power, and I many years ago demonstrated that certain samples of coal dust were explosive in the presence of air and in the absence of fire-damp.

The results of the analyses of the four resins are as follows:—

	Kilmarnock Coal.		Chemise Seam Coal	
	Soluble in Ether.	Soluble in Chloroform.	Soluble in Ether.	Soluble in Chloroform.
Carbon ..	84·275	74·281	57·497	66·700
Hydrogen ..	9·361	6·515	7·527	7·315
Oxygen. ..	6·364	19·204	34·976	25·985
	100·000	100·000	100·000	100·000

The only substances already described that we are aware of, and which are nearly of the same composition, are the mineral resins anthracoxenite and schlanite, as given in Dana's "Mineralogy" (pp. 745 and 746), and the analyses of which are:—

	Anthracoxenite. (Insoluble in Ether).	Schlanite. (Soluble in Ether).
Carbon ..	75·274	81·47
Hydrogen ..	6·187	8·71
Oxygen. ..	18·539	9·82
	100·000	100·00

Both substances are from the coal beds of Brandeisl, near Schlan, in Bohemia.

* Read before the Royal Physical Society of Edinburgh on Dec. 19, 1888, and illustrated by specimens.

This preliminary notice has been rendered necessary by the informal communication above quoted, and the author is now proceeding with the investigations of the resins obtainable from the coal measures.

PTOMAINES AND THEIR GENESIS, IN RELATION TO THE SEPSIN OF PANUM.

By JOHN M. WYBORN, F.C.S.

F. COPPOLA, while avoiding the conclusion that putrefaction is in no case sufficient of itself to cause the formation of the ptomaines, maintains that his researches have tended to show on the one hand that arterial blood contains no such alkaloids, and on the other that the processes, such as Dragendorff's, used for their extraction, are in themselves sufficient to produce them. These results are said to have been confirmed by the experiments of Marino, who was able to extract only traces of neurine and lecithin from various physiological products, and of Mosso and Guareschi, who state that in the extraction of alkaloids by sulphuric acid (Dragendorff's process), the substances owe their formation for the most part to the decomposing action of the acid.

Recently, however, it has been shown by V. Oliveri that the most dilute acids, even without the application of heat, cause the production of these substances from the decomposition of the lecithin and proteids present in the preparations. Moreover, the putrid solutions employed by investigators have been found to contain various acids, especially during the first fourteen days of the putrefactive process, and thus it would appear that this process itself is capable of producing the cadaveric alkaloids.

In 1865 Professor Panum, of Copenhagen, had demonstrated that albuminous substances yield by putrefaction a poisonous body soluble in water, insoluble in alcohol, and capable of withstanding a temperature of 100°. Bergmann has since confirmed this, and described the compound, *sepsin*, as generated by putrefaction.

By treating putrid infusion of muscle with strong alcohol, this substance has been obtained by Professor Burdon Sanderson* (who describes it as pyrogenous, or fever producing), Dr. Drysdale,† and others, and its poisonous characters have been verified.

In order to obtain a supply I proceeded as follows:—Lean beef, finely minced, was macerated in twice its weight of drinking water, without free access of air, but exposed on the sill of a window facing south to the heat and light of the sun during sixteen days (from 30th June, 1888) of dull, stormy weather with occasional sunshine. The strained liquid was then precipitated by an equal bulk of absolute alcohol. The precipitate was collected, boiled for five minutes in the same quantity of the alcohol as that first used, again collected and washed withboiling alcohol, and dried in a warm air chamber.

It was then extracted with distilled water and immediately filtered and evaporated to dryness on a water-bath. The residue, representing only 0·067 per cent. of the beef used, was found to consist of (1) a brownish red extract, rather heavy and freely soluble in water, (2) a pale greenish extract, very light and sparingly soluble in water, and (3) brilliant white crystalline plates.

Each grain (0·0648 grm.) of this residue was treated with 100 minims (5·9 c.c.) of a mixture of one volume of distilled water with two volumes of glycerin, forming, after standing, an amber coloured solution with a brown precipitate.

After keeping the solution one month, 5½ to 6 minims (0·324 c.c. to 0·354 c.c.), or less than $\frac{1}{10}$ grain of the extract, administered subcutaneously, was found to be fatal to mice in about an hour.

The filtered solution is at first nearly neutral to test-paper, but after exposure to the air it becomes strongly acid and acquires the odour of stale pepsin.

With platinic and auric chlorides precipitates are obtainable, but I regret that the quantity at my disposal is insufficient to admit of an analysis being made. It also gives precipitates with tannic, picric, phosphotungstic, and phosphomolybdic acids, that with the last named being sparingly soluble in ammonia.

With potassium ferrocyanide it gives a blue precipitate on the addition of ferric chloride, appearing after some time.

It also gives white precipitates with mercuric chloride and lead acetate, a yellow precipitate with potassium cadmium iodide, and a red precipitate with potassium bismuth iodide, and when boiled with potassium hydroxide an impure ammoniacal odour is observable.

Moist silver oxide digested with it is reduced to the metallic state.

With Nessler's reagent it yields a yellowish precipitate insoluble in dilute hydrochloric acid, and with Millon's reagent a white precipitate. Argentic nitrate causes a white precipitate insoluble in nitric acid, soluble in ammonia.

With acetic acid and potassium ferrocyanide a precipitate is obtained which is partially soluble in nitric and hydrochloric acids.

The dry residue when treated with sulphuric acid and potassium dichromate yields only a faint rose tint, which quickly vanishes. It is coloured yellow by nitric acid after standing for several hours.

From these reactions it would appear that while this body possesses many of the characters of the peptones, it also affords evidence of the presence of one or more of the cadaveric alkaloids, and such alkaloids must either be insoluble in alcohol themselves or in combination with some substance which renders them so, and, unless the alcohol were alone sufficient to produce them in the putrid solution, their pre-existence may be reasonably inferred.

† *British Medical Journal*, Feb., 1875, p. 201. *Ibid.*, Dec., 1877 p. 913.

* *On Pyrexin or Pyrogen.* By Dr. Drysdale. Baillière and Co.

SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,
Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

Introduction.

I.

PROFESSOR W. N. HARTLEY, of Dublin, being informed of my spectrum analysis of magnesium and carbon, drew my attention to the close relation existing between zinc, cadmium, and magnesium (pointed out in his paper "On the Homologous Spectra"), which seems to give evidence that these elements may be similarly composed. It might therefore be expected that my calculations for magnesium might easily be extended to zinc and cadmium.

This hint induced me to investigate the spectra of the latter elements. I began with the more complicated spectrum of cadmium, because I was convinced that the spectrum analysis of zinc would not cause me any further difficulty if I could succeed with the spectrum analysis of cadmium, as zinc takes the middle place between magnesium and cadmium in Mendeleeff's table of the chemical elements.

My investigations were successful in a degree I could never beforehand have ventured to hope. I succeeded not only with the analysis of cadmium here given, and later with the analysis of zinc in a relatively very short time, but I was also led by induction from these results to the

* A paper read before the Royal Society, December 13, 1888.

discovery of a very important relation between the structure of the elements and their position in Mendeleeff's table.

The analysis of cadmium and zinc showed first of all that these bodies, at least so far as their known spectra allow a conclusion, are composed of condensation forms (different states of condensation) of the primary elements "*a*," "*b*," and "*c*," which I first found in hydrogen [: volume formula : $H = ba_4$:], and in oxygen [: volume formulæ : $O = H'{\cdot}O'$, $O' = b_4O''_5$, $O'' = b_4c_5$; $O = H'{\cdot}b_4(b_4c_5)_5$:], then in magnesium and in carbon. (See *Astronomische Nachrichten*, 1887, No. 2797, or *Philosophical Magazine*, 1887, and my paper "Mathematische Spectralanalyse des Magnesium's und der Kohle" in the *Sitzungsberichte der Wiener Akademie*, 1887.

Between the divers condensation forms of the primary body "*b*" in cadmium and in zinc there is relatively one which is the strongest. The strongest condensation form of "*b*" in cadmium is $\frac{1}{2}$ times more condensed than that in which "*b*" occurs in the hydrogen bound in aqueous vapour, while the strongest condensation form of "*b*" in zinc is $\frac{1}{4}$ times as strong. As zinc belongs to the 5th, cadmium to the 7th series of Mendeleeff's table (but together with magnesium to the IInd group of it) the suggestion arises that the elements of the *n*th series of Mendeleeff's table (except perhaps the so-called "typical elements" of the 1st and 2nd series) may contain the primary element "*b*" in a state of condensation (probably the strongest amongst several condensation forms of "*b*" in the secondary element referred to), in which it may be $\frac{n}{n-1}$ times more strongly condensed than in the hydrogen of aqueous vapour.

Supposing this induction to be correct, there must occur amongst the rays of the secondary elements, especially amongst the most refrangible of them, some rays whose wave-lengths λ by multiplication with $\frac{n}{n-1}$ could be transformed in corresponding wave-lengths, $\frac{n}{n-1}\lambda$, of water vapour, at least for $n > 2$, and in the case that there are rays of sufficiently high refrangibility amongst those known. These rays, $\frac{n}{n-1}\lambda$, would belong to the primary body "*b*" in the same chemical state as in the hydrogen of aqueous vapour.

Well, the induction above mentioned could be proved in a clear manner by a great number of elements, viz., by the elements Al, Si of the 3rd series ($n = 3$), the element Fe of the 4th series ($n = 4$), the elements Cu, Zn, As, of the 5th series ($n = 5$), Sr ($n = 6$), the elements Ag, Cd, In, Sn, Sb, Te, of the 7th series ($n = 7$), Ba ($n = 8$), and the elements Au, Hg, Tl, Pb, Bi, of the 11th series.

According to this inductive law discovered by me, the secondary element, magnesium of the 3rd series, for instance, must possess, besides the four groups of rays already analysed by me, a hitherto unknown group of rays whose wave-lengths λ ($\lambda < 2605$) by multiplication with $\frac{1}{2}$ [: $\frac{n}{n-1}$ for $n = 3$:] will be reduced to wave-lengths $\frac{1}{2}\lambda$ of the water spectrum, forming a special group of the very numerous group (H_2O, O, *b*), due to the primary body "*b*" in the hydrogen of aqueous vapour. A similar prediction can be made concerning the rays λ of the other elements of the 3rd series, viz., Na (Al, Si, see above), P, S, and Cl; each element of the 4th series ($n = 4$), viz., K, Ca, Sc, Ti, V, Cr, Mn (Fe, see above), Co, Ni, will have respectively one group of more refrangible rays, the wave-lengths of which will be transformed by multiplication with $\frac{1}{2}\left(\frac{n}{n-1} \text{ for } n = 4\right)$ to wave-lengths, $\frac{1}{2}\lambda$ of the water vapour, forming also different partial groups of the group (H_2O, H, *b*) above mentioned, and so on.

"The wave-lengths due to homologous groups of different elements of the same group in Mendeleeff's table are connected, as I have further found, with their atomic weights, generally three and three, by very remarkable relations." The full exposition of those relations is reserved for a later special publication, which will be accompanied by very extended tables giving the evidence of them. I hope that in the meantime the predictions above made upon the ground of the fore-mentioned inductive law will be at least partially confirmed by future measurements, and that I shall be thus enabled to complete the induction by a further set of elements.

II.

But still in another direction scarcely less important, the spectrum analysis of cadmium, and especially that of zinc, together with the comparison of their spectra, have been of great consequence for the progress of my researches, as they confirmed me in the suggestion that the primary element "*c*" of oxygen (found also in Mg and in C, besides the primary element "*b*") "might be no other than a certain condensation form of the primary element '*a*' of hydrogen $H = ba_4$)."

(α) The electropositive character of the elements of the first of Mendeleeff's groups, and the same character of the primary body "*a*," the chemical analogy of the latter with the former and with the radicle "ammonium," NH_4, seemed to me to give some ground for the inference that condensation forms of the primary body "*a*" with and besides condensation forms of the primary body "*b*" might take a prominent part in the building up of the elements of Mendeleeff's first group in such a way that these elements might be looked upon as ammonium-like compounds of radicles, viz., of one radicle pentavalent (relatively 3-valent) and of four radicles monovalent, which might be, in general, compounds of the primary bodies "*a*" and "*b*," if not identical with the latter.

(β) The close relations which exist according to the inductive law above mentioned between the primary element "*b*" and the most refrangible rays of the secondary elements, together with the chemically different, nay contrarious, character of the bodies "*a*" and "*b*," made it probable that there might be also close relations between the primary element "*a*" and the least refrangible rays of the secondary elements.

Both reflections [: quoted above sub (α) and (β) :] induced me to examine whether the least refrangible rays of Li, Na, K, &c., at present known belong or do not belong to condensation forms of the primary element "*a*," and whether they are due directly or not to certain condensation forms of the primary element "*c*." Suppose the answer to be affirmative in each case—then it could not be difficult to determine the reduction factor for the transformation of the wave-lengths due to the primary body "*c*" into wave-lengths due to the primary body "*a*" in a definite chemical state, for instance, in that occurring in free hydrogen.

Success justified and confirmed my suggestion. The red rays of kalium, for instance, observed by Kirchhoff, Mascart, Huggins, Lecoq, Liveing and Dewar, Roscoe and Schuster, belong for the most part at the same time to a certain condensation form of the primary element "*a*," and to another definite condensation form of the primary element "*c*," their wave-lengths being rhythmically connected with the wave-lengths of "*c*," and with the wave-lengths of "*a*" in the same chemical state as in free hydrogen.

"The primary element '*c*' of oxygen, magnesium, and carbon is therefore no other than a definite condensation form of the primary element '*a*' of hydrogen, $H = ba_4$."

Now in all secondary elements, the spectra of which I have hitherto analysed, in O, Mg, C, Cd, and Zn I have met, besides the primary bodies "*a*" and "*b*," only with the primary body "*c*" occurring in different chemical states.

As "*c*" is recognised to be a certain condensation form of "*a*," the fore-mentioned secondary elements will only

be composed of condensation forms of the two primary elements "*a*" and "*b*." This result leads us to the empirical induction that perhaps all the known and unknown secondary elements of Mendeleeff's table may be built up (besides the all-penetrating ether) of condensation forms of the two primary bodies "*a*" and "*b*," and may therefore (in the last instance) be only compounds of the latter.

If this inductive law should be proved true by further researches, Prout's hypothesis (*Annals of Philosophy*, by Th. Thompson, 1815 (6), 321) would have to be replaced by the following law:—

"The atomic weights of all secondary elements can be derived from the atomic weights of the two primary components "*a*" and "*b*" of hydrogen, $H = ba_4$, by integral numbers; the atomic weight of a secondary element, which consists in the last instance of α-atoms "*a*" and β-atoms "*b*," being given by the expression $a\alpha+\beta b$.*

The above results open up a magnificent prospect upon a very wide field for further research, and point to very important objects—immeasurably distant, it is true, but well defined in their outlines—for the co-operation of physics, chemistry, and astronomy (astrophysics).

The full exposition of the interesting relations here briefly sketched I reserve for a later publication.

III.

I have found by my spectrum analyses, that to the same condensation form of a primary element, occurring in different secondary elements, belong different partial groups of wave-lengths; these groups being in the same rhythmical relations to other comparison spectra, especially to that of aqueous vapour, but having besides almost nothing in common one with another.

With regard to the great importance of the forementioned partial or special groups for the comparison of the spectra, produced by different bodies, I may be permitted to elucidate their intrinsic meaning by a plain comparison:—

When an element occurs in two different bodies in the same chemical state [for instance, the primary body "*b*" in the state (H,*b*), such as it occurs in free hydrogen, in the magnesium and in carbon], the physical state of it is nevertheless by no means the same in the different bodies.

The various physical states of the same chemical condensation form in various bodies can be compared in a very striking manner with the various physical states or modifications a plate of the same metal undergoes, if it is wrought into different forms, variously supported and then variously rubbed or beaten.

As plates of the same kind of matter by such varied manner of treatment can be put into various systems of vibrations, with various systems of nodes, consequently in various physical modifications, while in the same chemical state, so the same chemical condensation form of an element can be set in various peculiar systems of vibrations, if it is combined with various other elements in different bodies, and therefore rubbed by various systems of waves excited in the surrounding ether or variously beaten by the atoms (or molecules) of the other components; systems of vibrations, which in return will be impressed on the surrounding ether, and brought to our knowledge by the latter.

I call the whole of all possible vibrations that a gaseous element in the same chemical state, but under various physical circumstances may assume, "the vibration complex due to that chemical state or condensation form;" and the whole of correspondent waves produced by it in the surrounding ether, "the complex of rays due to it."

This comprehension of all possible special groups, due to a certain condensation form of a gaseous element, into a "complex," is, however, only an ideal one; and it is therefore to be noted, that the mentioned condensation form cannot synchronously execute all the vibrations of the complex ideally (in imagination) due to it; in so far as the various physical conditions, which determine the appearance of the various special groups contained in the "complex," can either not exist together, or can only partly and under special conditions exist simultaneously. The foregoing exposition characterises in a sufficient manner the actual state of my spectral-analytical researches concerning the application of my theory to the discussion of the spectra.

IV.

The present paper on cadmium is a very remarkable link in the chain of publications intended to give an account of my results. It contains only a further instructive and interesting application of the criteria already known for the recognition of the primary elements "*a*," "*b*," and "*c*," which I have published in my paper, "Ueber die merkwürdigen Beziehungen zwischen dem Spectrum des Wasserdampfes und den Linienspectren des Wasserstoffs und Sauerstoffs, &c.," in the *Astronomische Nachrichten*, 1887, No. 2797, (also *Phil. Mag.*, 1887), and which I have arranged together in my paper, "Mathematische Spectralanalyse des Magnesium's und der Kohle," pp. 2—5.

The scale to which all wave-lengths in my paper are referred is that of Angström when no other scale is especially indicated. The numbers given on Angström's scale can easily be reduced to the corresponding numbers given on Rowland's or on Müller and Kempf's scale by the comparison of the relative wave-lengths of the solar lines E_1, E_2; at least so far only the systematic relations of the three scales are taken into consideration.

The wave-lengths of the above mentioned lines E_1 and E_2 are according to Angström ("Recherches sur le spectre solaire, spectre normal du soleil," Upsala, 1868); Henry A. Rowland ("On the Relative Wave-lengths of the Lines of the Solar Spectrum," *Phil. Mag.*, vol. xxiii., 1887); and Müller and Kempf ("Publikationen des Astrophysikalischen Observatorium's zu Potsdam," 1886):—

⊙	Angstrom's scale.	Rowland's scale.	Müller and Kempf's scale.
E_1	5269·59	5270·43	5270·53
E_2	5268·67	5269·65	5269·80

From these numbers we derive—

$$\left.\begin{array}{l}\text{For } E_1: 5270{\cdot}43 : 5269{\cdot}59 = 1{\cdot}00016\\ \text{For } E_2: 5269{\cdot}65 : 5268{\cdot}67 = 1{\cdot}00018\end{array}\right\},$$

therefore in the mean—

$$\frac{1{\cdot}00016+1{\cdot}00018}{2} = 1{\cdot}00017 = 1-\frac{1}{6000}$$

is the systematic reduction-factor for the transformation of the numbers on Angström's scale into the corresponding numbers on Rowland's scale, and $1-0{\cdot}00017 = 1-\frac{1}{6000}$ is the reduction-factor for the change of the latter to the former:—

Further for—

$$\left.\begin{array}{l}E_1: 5270{\cdot}53 : 5269{\cdot}59 = 1{\cdot}00018\\ E_2: 5269{\cdot}80 : 5268{\cdot}67 = 1{\cdot}00022\end{array}\right\},$$

thus, in the mean $\frac{1{\cdot}00018+1{\cdot}00022}{2} = 1{\cdot}00020$ is the systematic factor for the reduction of the numbers on Angström's scale into the corresponding numbers of Müller-Kempf's scale, and *vice versâ*: $1-0{\cdot}00020$ is the factor for the transformation of the latter into the former.

We can express hereafter the systematic relations between the three scales (with an accuracy sufficient for our purposes) by the equations:—

* Prout, not knowing hydrogen to be a compound, suggested that this element, on account of its physical and chemical properties, especially its low atomicity and its almost exact multiple relations with many elementary substances, might be the ponderable base of all the others. *Annals of Philosophy*, vol vi., p. 330 (1815); vol. vii., p. 113 (1816).

$$\begin{cases} \lambda\ (R)=\lambda(A)+\frac{1}{6000}\lambda(A)\,;\ \lambda(A)\ =\lambda(R)-\frac{1}{6000}\lambda(R), \\ \lambda\ (M.K)=\lambda(A)+0{\cdot}00020\,\lambda(A)\,;\ \lambda(A)=\lambda(M.K)-0{\cdot}00020\,\lambda(M.K), \\ \lambda\ (M.K)=\lambda(R)+0{\cdot}00003\,\lambda(R)\,;\ \lambda(R)=\lambda(M.K)-0{\cdot}00003\,\lambda(M.K), \end{cases}$$

where λ (A), λ (R), (λ M.K) denote relatively the wave-length of one and the same ray on Angström's, Rowland's, and Müller-Kempf's scales.

The symbols used by me to denote the various condensation forms of the primary bodies occurring in H and O, &c., and the groups of wave-lengths due to it, are the same as in my paper on Magnesium and Carbon.

Thus denote, for instance, by—

(H, *b*) the group of wave lengths due to the primary body "*b*" in the chemical state, in which it occurs in free hydrogen.

(O, O', *b*) the group emitted by the primary element "*b*" in the chemical state, in which it occurs in the component $O' = b_4O''_5$, contained in free hydrogen $O = H'O'$; H' being the modified hydrogen which produces the second or so-called compound spectrum (H') of hydrogen.

(O, O', O'', *b*) the group, emitted by "*b*" in the same chemical state as in $O' = b_4c_5$, a component of $O'=b_4O_5$ in free oxygen $O=H'O'$.

(O, O', O'', *c*) the group, emitted by the primary body "*c*" in the chemical state, in which it occurs in free oxygen, producing there the rays—

6146·0	H. H. Vogel.	4754·0	Plücker.
5205·4	Schuster.	4750·1	Schuster.
5190·0	,, (Plücker, Huggins).	4711·0	Plücker.
		4709·0	Schuster.
5175·4	,,	4705·0	Schuster, Huggins.
5159·3	,,	4699·0	Huggins (4698·5 Schuster).
5144·0	Plücker.		
4953·0	Huggins.	4695·5	Schuster.
4942·2	Schuster.	4690·0	Plücker.
4940·2	,,	4677·0	Huggins.
4923·7	,,	4675·4	Schuster.
4907·0	Huggins.	4660·7	,,
4892·0	,,	4649·3	,,
4890·0	Schuster.	4640·6	,,
4884·0	Plücker.	4639·0	Plücker.
4871·0	Schuster.	4600·0	,,
4866·0	Plücker.	4595·1	Schuster.
4864·0	Schuster.	4588·0	Huggins.
4863·0	H. C. Vogel.	4475·0	Salet.
4860·2	Schuster.	4469·2	Schuster.
4856·2	,,	4465·0	,,
4853·0	Huggins.	4455·0	Salet.
4848·0	Plücker.		&c.,

As it is very probable that several wave-lengths, found by calculation in the course of my discussion of the cadmium spectrum, and due to various condensation forms of the primary elements (especially of "*b*" in hydrogen or oxygen) may be met with in certain spectra—it is worth while to compare them with the latter. Thus, I should recommend—

(1). The comparison of the calculated wave-lengths due to the group (H, *b*) with the hydrogen spectrum, with the solar spectrum, with the star spectra (especially with that of the white stars), and with the spectrum of the oxy-hydrogen flame.

(2). The comparison of the calculated wave-length belonging to the groups (O, O', *b*), (O, O', O'', *b*), O, O', O'', *c*) with the oxygen spectrum, the air spectrum, the spectrum of the oxyhydrogen flame, &c.

For the sun and the stars possessing a light of their own (principally the white stars), contain in their outer atmospheres immense masses of burning and glowing hydrogen; they contain, and emit therefore certainly also, the most rays due to the primary bodies "*a*" and "*b*" in the same chemical states as in hydrogen, amongst the rays of their spectra.

The oxyhydrogen flame contains, at least among the rays less refrangible rays than λ 3300, several rays of incandescent hydrogen and oxygen amongst the mass of rays due to the aqueous vapour though of very small intensity, and in general quickly fading away as the refrangibility increases.

I have for this reason made the fore-mentioned comparisons, and have expressed their results in the tables.

The lines of the water spectrum (principally used as a comparison spectrum) are taken partly from the observations of Huggins (*Proceedings of the Royal Society of London*, 1880), "On the Spectrum of the Hydrogen Flame," partly from the *Report of the British Association*, 1886, pp. 169—171; for the most part, however, from the epistolary communications of Professor G. D. Liveing, of Cambridge.

During the elaboration of my paper on magnesium and carbon these communications reached only to the 13th September, 1887, but I was afterwards, by means of a communication of 24th January, 1888, enabled to use also the most recent measurements of Messrs. G. D. Liveing and J. Dewar, by which the former have been partly corrected and amplified; still this was antecedent to their publication in the *Philosophical Transactions of the Royal Society*, 1888, pp. 27—42 ("On the Spectrum of the Oxy-hydrogen Flame").

In some cases where the rays of the water spectrum are too weak to act upon the photographic plate, I carried the comparison with the very numerous group of wave-lengths $\frac{H'}{2}$, corresponding to the wave-lengths H' of the second or so-called "compound line spectrum of the hydrogen," the former being the halves of the latter. The wave-lengths H' used were those measured by Dr. B. Hasselberg, of Pulkova, with great accuracy and with exemplary circumspection, originally in 1882, then with better instruments, and therefore with still greater accuracy and more in detail, 1883 and 1884. (See the *Mémoires de l'Academie de St. Pétersbourg*, "Untersuchungen über das H. Spectrum des Wasserstoffs," 1. Abhandlung 1882, 2. Abhandlung 1883, and "Zusatz zu meinen Untersuchungen," &c., 1884.

It may be still especially remarked that the most refrangible section of the water spectrum from λ=2448·4 to λ=2268·0, as also the least refrangible from λ=3673·3 to λ=4265·0 are so faint that Liveing and Dewar are compelled to expose the photographic plate up to five hours in order to make the whole of the lines visible and measurable, and to prove the existence of several lines predicted by me. The wave-lengths thus found are therefore liable to greater errors of observation than the others. These circumstances account also for some gaps occurring in some comparisons corresponding to certain criteria, and caused by the rays being too faint to be measurable, though the existence of such rays is notwithstanding ascertained by their satisfying other criteria.

Spectrum Analysis of Cadmium.

The lines corresponding to the rays of cadmium hitherto known can be distributed into six groups, whose wave-lengths can be characterised by their rhythmical relations to other spectra, especially to the water spectrum.

Each wave-length λ of this group can be reduced by multiplication with $\frac{2}{3}$ to wave-length $\lambda'=\frac{2}{3}\lambda$, which can be recognised as due to the primary body "*c*" in the same chemical state as in oxygen or in magnesium by the criteria given in my paper, *Mathematische Spectralanalyse des Magnesium's und der Kohle*, p. 4, sub. III., and p. 5, sub. VI., viz.:—

$\frac{2}{3}\lambda'$ is a wave-length of a ray of aqueous vapour, produced by the primary body "*c*" in the chemical state in which it occurs in the oxygen of water vapour; thus a wave-length of the group (H_2O, O, O', O'', *c*) [first chief criterion]; further—

The Ist group of cadmium-rays is—

λ =	6742·0	Kirchhoff.
	6740·0	Huggins.
	6726·5	Kirchhoff.*
λ =	6468·0	Kirchhoff.
	6466·0	(?) broad, Thalén's, seems to be too small by two units.
	6462·0	Huggins.
	6056·5	Thalén.†
	5958·0	Huggins.†

$\frac{1}{3}\lambda'$ is a wave-length of the group (H_2O, O, O′, O″) of the water spectrum, produced by the body $O'' = b_4c_5$ in the same state as it occurs in the oxygen ($O = H'_2b_4O''_5$) of the aqueous vapour (second criterion); finally—

$\frac{2}{3}\lambda'$ is one of those wave-lengths of the water spectrum into which the wave-lengths of oxygen can be transformed by multiplication with $\frac{2}{3}$, the mean condensation factor of O and H in their union to form water vapour (third criterion).

Table I. gives a view of the characteristic relations just mentioned. The first column contains the wave-lengths λ of the Ist group; the second, the wave-lengths of the "*c*" rays rhythmically corresponding; the third and fourth, the fifth and sixth, finally the seventh and eighth columns give evidence of the accuracy with which the single rays of the group satisfy relatively the first, second, and third criterion. The wave-lengths satisfying all criteria with great accuracy, give first-rate evidence of the real existence of the group.

The Cd ray λ = 6740 (Huggins), which satisfies only the first and third criterion, leads by the second criterion to a new, very faint, still unknown line of aqueous vapour about λ = 2808·3. The Cd ray λ = 6056·5 (Thalén) is an empirical nodal ray (or ray of ramification) of the Ist and IInd group. Also the Cd ray about 5958 (Huggins) could be considered as an empirical nodal ray of the first two groups, but it seems to me to be more probable that it is only one of two faint rays lying close together and forming the nebulous ray of Thalén about 5957·5, and having the approximate wave-lengths 5958 and 5957·5, due respectively to the Ist and the IInd group. For while λ = 5958 satisfies the criteria of the Ist group very well, λ = 5957·5 answers better to the most part of the criteria of the IInd group. (See the latter).

The wave-length λ = 6466 of the broad cadmium-ray of Thalén, answering evidently to the Cd ray λ = 6468 of Kirchhoff, seems to be too small by almost two units, as Kirchhoff's 6468 answers exceedingly well to the three criteria of the Ist group, while Thalén's λ = 6466 does not satisfy the first and the third criterion.

Cadmium contains, therefore (according to my well-known fundamental theorem), the primary body "c" in a chemical state, dilated in the ratio 3 : 2 in comparison with the state in which "c" occurs in the oxygen or in magnesium.

The wave-lengths λ of the above group are changed by multiplication with $\frac{2}{3}$ into wave-lengths $\lambda' = \frac{2}{3}\lambda$, which answer to the criteria for the wave-lengths (H, *b*), due to the primary element "*b*" in the same chemical state as in hydrogen, and given in my paper, *Mathematische Spectralanalyse des Magnesium's und der Kohle*, on p. 3, sub. II., and on p. 5, sub. VI.; they form, therefore, a special group of the wave-lengths complex (H, *b*).

According to these criteria there corresponds rhythmically to each wave-length λ, due to that group (H, *b*), four wave-lengths:—

$\frac{1}{3}\lambda'$, $\frac{2}{3}\cdot\frac{4}{5}\lambda'$, $\frac{2}{3}\cdot\frac{7}{8}\lambda'$, and $\frac{2}{3}\lambda'$ of the water spectrum

* Probable value. Kayser in his *Lehrbuch der Spectralanalyse*, Berlin, 1883, p. 254, gives for this ray λ = 6726, whereas the *British Association Report*, 1887, p. 368, gives for it λ = 6727.

† The lines 6050 and 5959 given by Kayser, as observed by Huggins, are not to be found in the original paper of Huggins, "On the Spectra of Some Chemical Elements," *Phil. Trans.*, 1864; but instead of those, there occur the lines 6056 and 5958. The two former may therefore be misprints.

The IInd group of the cadmium-rays contains the rays—

λ =		
6438·0	very strong, Thalén.	
*6056·5	very strong, nodal ray of the Ist and IInd group.	
6004·0	Huggins (6003·5 Thalén).	
5957·5	nebulous, Thalén.	
5913·5	mean value of	5914 Huggins. 5913 Thalén.
5790·0	nebulous	Thalén.
5687·0	nebulous	
5489·0	nebulous	
5471·0	nebulous	
5379·9	Kirchhoff	
5378·0	very strong, broad, nebulous, Thalén.	
5377·0	Huggins, Mascart.	
5339·0	Kirchhoff.	
5337·5	very strong, very broad, nebulous, Thalén.	
**5337·0	Kirchhoff, nodal ray of the IInd and IVth group.	
5304·5	Thalén (5304 Huggins).	
**5153·0	Thalén, Huggins; nodal ray of the IInd and IVth group.	
5086·0	(better than 5085 Thalén).	
5084·0	(?) Mascart.	
4799·0	Hartley and Adeney.	

and two wave-lengths, $\frac{2}{3}\frac{8}{9}\lambda'$ and $\frac{2}{3}\frac{9}{10}\lambda'$, of the oxygen spectrum, answering to the second and third of the four above-stated wave-lengths.

(1). $\frac{2}{3}\lambda'$ is a wave-length due to the condensation form H, *b*) of the primary body "*b*," in the same state as in hydrogen in water vapour (first or chief criterion).

(2). $\frac{2}{3}\cdot\frac{8}{9}\lambda'$ is a wave-length which proceeds from the condensation form (H_2O, O, O′, *b*) of the primary body "*b*" in the compound O′ of O, bound in H, O vapour (second criterion).

(2*a*). $\frac{2}{3}\frac{8}{9}\lambda'$, being a wave-length due to the chemical state (O, O′, *b*) of "*b*," as contained in the component O· of free oxygen (first accessory criterion).

(3). $\frac{2}{3}\cdot\frac{9}{10}\lambda'$ is a wave-length belonging to the chemical condensation form (H_2O,O,O′,O″,*b*), thus produced by the primary body "*b*" in the state in which it occurs in $O'' = b_4c_5$, and with it in the oxygen of aqueous vapour (third criterion); while—

(3*a*). $\frac{2}{3}\frac{9}{10}\lambda'$ is a wave-length generated by the primary element "*b*" in the chemical state (O,O′,O″,*b*), occurring in the component $O'' = b_4c_5$ of $O' = b_4O''_5$, in free oxygen, O = H′O′, under proper physical conditions (second accessory criterion; finally—

(4). $\frac{2}{3}\lambda'$ is one of those wave-lengths of aqueous vapour, to which the wave-lengths of hydrogen therefore, also the wave-lengths of the condensation form (H,*b*)] can be reduced by multiplication with $\frac{2}{3}$, the mean reduction factor of H by its union with oxygen to form aqueous vapour.

The rays of the IInd group have, therefore, the character of helium-rays, being produced by the primary body "*b*" in the chemical state into which it comes when the hydrogen begins to be dissociated and simultaneously expanded in the ratio 2 : 3.

The Tables II., II.*a*, II.*b*, II.*c*, show in how great a degree the criteria above mentioned are satisfied by the rays of this group, and especially by those due to the wave-lengths.

It should be particularly noted that the first columns of the Tables II.*a*, II.*b*, II.*c*, coincide with the second column of the Table II., forming thus branches of the latter. The ray λ = 6056·5 (Thalén) is a nodal ray of the Ist and IInd groups; the ray λ = 5337 (Kirchhoff) and 5153 (Thalén) are nodal rays of the IInd and IVth groups. Thalén's λ = 5085 seems to be only the mean of two closely united lines at λ = 5086 and λ = 5084, appearing as one very strong line, as the latter satisfies with great accuracy the first three criteria; presupposing that

Mascart's 5084 is not also an erroneously determined value of $\lambda = 5086$.

"Cadmium contains thus, according to the above discussion, the primary body "*b*" of hydrogen in the same chemical state as in helium, *id est*, in the state into which "*b*" comes when free hydrogen begins to be dissociated by sufficiently elevated temperature (and perhaps also by at the same time suitably diminished pressure), expanding itself simultaneouly in the ratio 2 : 3."

(To be continued).

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

In accordance with the call of the Secretary, the Association met in the library of the Department of Agriculture at 10 o'clock on Thursday, August 9, the President, Mr. P. E. Chazal, in the chair.

The President, in calling the meeting to order, said that he would omit the usual address, as there was a desire to proceed at once to business, with the view of accomplishing the objects of the convention in as short a time as possible.

On a call for reports of committees, Mr. Richardson, in the absence of the chairman, presented the report of the Committee on Cattle Foods.

Dr. Wiley then presented the Report of the Committee on Dairy Products, as follows :—

Report of the Committee on Dairy Products.

Mr. President—I found it impracticable to secure a meeting of the committee appointed at the last meeting to consider the subject of dairy products, and have therefore no report considered by all of the members of the committee to present. In the absence of such a document I thought it best to submit a brief résumé of the work which has been done in dairy products during the year since our convention last met. The methods proposed at our last meeting for the analysis of dairy products have given fairly good satisfaction, and I therefore recommend that they be continued unchanged for another year. Many points which are now in dispute will have been settled by that time, and at our next annual meeting any necessary changes in methods of analysis can be made.

With this introduction I beg to submit the following abstracts of the progress made in the analysis of dairy products during the year just past.

Milk Analysis.

Use of Asbestos Cloth Instead of Blotting-Paper in the Adams Method.

Johnstone has reported to the Society of Public Analysts favourable results attending his experiments in substituting asbestos paper for blotting-paper in the Adams method of fat estimation.—(Abstract from the *Analyst*, December, 1887, p. 234.)

(Note.—I called attention to the use of asbestos paper for this purpose two years ago, as will be seen on page 81 of *Bulletin* No. 13, Part 1.)

An Instrument for Calculating Milk Results.

Richmond has described an instrument for calculating milk analyses based on the relations existing between fat, solids not fat, and specific gravity in milk as established by the paper of Hehner and Richmond, published in the *Analyst*, vol. 13, p. 26. The instrument consists of a slide rule, on one side of which a scale, of which one division equals 1 inch, represents total solids. The other scale, one division of which equals 1·164 inches, represents the fat; while the scale representing specific gravity has a division equal to 1·254 inches.

The instrument is based upon the formula $T - 0{\cdot}254\ G = 1{\cdot}164\ F$. To use the instrument the lines indicating total solids and specific gravity found by analysis are placed together. The fat is then read off by an arrow on the other side. Where many analyses are to be made the instrument is especially valuable, since it eliminates all chances of error in calculation.—(Abstract from the *Analyst*, 1888, vol. 13, No. 144, p. 65.)

Estimation of Fat in Milk and Cream.

Werner Schmid proposes the following method of estimating milk fat: A test-tube of about 50 cubic centimetres capacity is graduated in tenths of a cubic centimetre; 10 cubic centimetres of milk or 5 cubic centimetres of cream are placed in the tube, and 10 cubic centimetres concentrated hydrochloric acid. The contents of the tube are boiled with constant shaking until the liquid is dark brown. After cooling in water add 30 cubic centimetres ether; shake, allow to stand until the ether solution has separated, measure its volume and remove 10 cubic centimetres with a pipette; place in a porcelain crucible, evaporate, and dry at 100° in air-bath. Calculate to total volume of the ether solution. The results are said to be exact.—(*Zeit. Anal. Chem.*, 27, p. 464.)

The Relation of Specific Gravity, Fat, and Solids not Fat, in Milk.

Hehner and Richmond have made an exhaustive study of the relations existing between the specific gravity, fat, and solids not fat, in milk. Three sets of determinations of the fat were made, viz., extraction from a paper coil, from plaster of Paris, and the direct extraction of the dried total solids. All previous formulæ relating to the above relations have been based upon imperfect methods of fat extraction. The work of Hehner and Richmond is therefore especially valuable on account of being based upon the Adams method of extraction. Forty-two analyses of various kinds of milk were made. For discussion of the formulæ the original paper is cited. The working formula obtained is $T - 0{\cdot}254\ G = 1{\cdot}164\ F$.

A table accompanying the paper gives the percentage of fat, calculated for specific gravities ranging from 1024·0 to 1034·0, and for total solids from 10 per cent to 15 per cent, inclusive.

The author strongly recommends that no milk analyses be accepted as correct which do not correspond closely with the calculated results.—(Abstract from the *Analyst*, vol. 13, No. 142, p. 26.)

Sources of Error in Soxhlet's Method of Estimating Fat in Milk.

Weinwurm has determined the error which may arise by allowing the ether fat solution obtained by Soxhlet's method to stand for varying lengths of time before its specific gravity is determined. As a result of his experiments, it appears that the apparent percentage of fat is raised by allowing the solution to stand for a long time. For the first twenty-four hours, however, this increase is only small, the amount, at most, being a few hundredths of a per cent. By standing a long time the apparent percentage of fat gradually increases, and appears to reach a maximum at the end of ten days. The amount of increase in that time may be 0·25 of 1 per cent.—(Abstract from Repertorium No. 19 of the *Chemiker Zeitung*, 1888, p. 151, and *M. Zg.*, 1888, 17, p. 401.)

Estimation of Dry Substance and Fat in Milk by Means of Wood Fibre.

Gantter proposes the use of wood fibre for the estimation of fat in milk, which he uses as follows :—

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

Two grms. of wood fibre are dried at 105° to constant weight in a dish containing a small glass rod. The total weight of the dish, glass rod, and fibre is noted. After weighing the dish, which is covered with a neat-fitting cover to prevent the absorption of water, 5 to 6 grms. of the milk are poured upon the wood fibre, and the exact amount taken determined by re-weighing the bottle. During evaporation the mass of fibre is pressed from time to time against the sides of the dish, so that no particles thereof remain attached thereto. The final drying is made in an air-bath, and the whole time required for the evaporation and drying should be about two hours and a half. From the increase in weight the amount of dry substance is determined. The mass of fibre is now transferred to a Soxhlet extraction apparatus, and, if necessary, the dish rinsed with petroleum ether. The extraction of fat and the weighing thereof are carried on in the usual way. The author has also used this method for the determination of water in butter and other fats and oils.—(Abstract from the *Zeitschrift für analytische Chemie*, vol. 26, No. 6, p. 678.)

The Chemical Action of Some Micro-Organisms in Milk.

Warington has studied the effect of certain micro-organisms on the curdling of milk. This curdling is effected either by the formation of a rennet-like ferment or by the production of lactic acid. The amount of lactic acid required to curdle milk depends on the temperature, the amount growing less as the temperature rises. Five different organisms were examined which had the power of curdling milk, but in very different degrees. They were *Staphylococcus candidus; B. termo; M. gelatinosus, B. fluorescens liquescens*, and *M. ureæ*.

Some of them readily curdled milk at a temperature as low as 10°. They do not, however, at that temperature produce an appreciable acidity. They therefore act plainly as a ferment. A large quantity of gas is evolved during the action of the same on milk.

Five organisms were also found to act as peptonisers; they are, *B. subtilis, B. anthracis, B. floccus, B. toruliformis*, and Finkler's comma. The milk treated with these organisms at 22° becomes clear after a few days. The clear fluid is rich in pepton. A few organisms render milk after a time decidedly alkaline; two of these are, *B. fluorescens non liquescens* and the *Bacillus of septicæmia*.

Cultivation in milk is an excellent method of distinguishing micro-organisms. — (Abstract from the Chemical News, June 22, 1888.)

Reduction and Rotation Power of Milk Sugar.

Deniges and Bonnans have reviewed the literature concerning the reduction of copper solution by milk sugar. As compared with pure glucose the reducing power of lactose is as 96 to 136. The copper solution employed contained 34·65 grms. of pure crystallised copper sulphate and 10 cubic centimetres pure sulphuric acid per litre. The alkaline solution was composed of 250 cubic centimetres of soda lye of 36° strength, in which was dissolved 150 grms. of crystallised Rochelle salts. Ten cubic centimetres of this solution was added to each 10 cubic centimetres of the copper solution.

For the determination of the rotatory power of lactose the author used a pure sugar, obtained by three crystallisations. The specific rotatory power for the anhydrous sugar at 20° was 55·30 for concentrations varying from 4 to 36 per cent; for the crystallised sugar the specific rotatory power in the same condition is 52·53. The general formula for the crystallised salt would be $[a] = 52{\cdot}53 + (20 - T) \times 0{\cdot}055$. The number 0·055 is the correction to be applied for each variation of 1° in temperature. The numbers obtained by the authors are exactly those given by Schmöger.—(Abstract taken from the *Journal de Pharmacie et de Chimie*, April and May, 1888, pp. 363 and 411.)

Estimation of Sugar in Milk by the Polariscope.

Vieth discusses the method adopted by the Association of Official Agricultural Chemists for the estimation of sugar in milk, which was originally described by me in the *American Chemical Journal*, vol. vi., No. v. The author is of opinion that acetic acid and subacetate of lead can be used with equal advantage with mercuric nitrate and nitric acid for preparing the milk for polarisation. He, however, prefers the use of the mercury salt. He calls attention to the correction which should be made in the reading of the polariscope for the volume of the precipitate. According to Vieth this correction in the method adopted by the Association is too small. The volume of the precipitate is equal to the combined volumes of the precipitated casein and fat carried down with it. The method employed by Vieth for making the correction for the volume of the precipitate is illustrated by the following example:—

Given a milk with a specific gravity of 1·0325 which contains 3·72 of fat. Add to 50 cubic centimetres of this milk 1½ cubic centimetres of the mercuric nitrate solution. The polarisation of the filtrate shows 5·1 milk sugar. The necessary calculations for the correction of this number are as follows:—

$$93 : 100 :: 372 : X \text{ whence } X = 4$$

the volume occupied by the fat.

$$103{\cdot}25 : 96 :: 51 : X \text{ whence } X = 4{\cdot}74.$$

The number 96 in the above formula represents 100 c.c. of the liquid less 4 c.c., the volume of the fat. The number 4·74 represents the percentage of crystallised milk sugar. The percentage of the anhydrous milk sugar would therefore be 4·5.—(Abstract from the *Analyst*, vol. xiii., No. 144, p. 63).

Short's Method of Determining Fat in Milk.

(Bul. Wis. Ag. Ex. Station, No. 16.)

The process depends on the following facts: That when a mixture of milk and a strong alkali is heated to the temperature of boiling water for a sufficient time the fat of the milk unites with the alkali and forms a soap which is dissolved in the hot liquid; at the same time the casein and albumen are disintegrated and become much more easily soluble. After the heating has continued for about two hours the mixture of milk and alkali becomes homogeneous and of a dark brown colour. On the addition of an acid the soap is decomposed, the fatty acids are set free, and rise to the surface, while the albumen, casein, &c., are first precipitated and then dissolved. The insoluble fatty acids thus obtained constitute very nearly 87 per cent. of the total fat of the milk.

Apparatus.

The process requires the following apparatus:—

(1) Tubes made of soft lead glass about one-sixteenth inch thick. The lower part of the tube is about 5 inches long and fifteen-sixteenths of an inch in diameter. The upper part of the tube 5 inches long and one-fourth inch inside diameter.

(2) Three pipettes, one holding when filled up to the mar7 on the neck 20 cubic centimetres (about two-thirds of an ounce), this being the exact amount of milk to be taken for analysis; the other two pipettes, holding 10 cubic centimetres each, for measuring the alkali and acid used.

(3) A scale, divided in millimetres, for measuriug the column of fat when the analysis is finished. The one used by the writer is a folding boxwood rule, but any rule divided in millimetres will answer the purpose.

(4) A water-bath made of sheet copper. It is provided with a rack to hold the tubes while being heated; also a feed and overflow to keep the water in the bath at a constant level.

(5) A wash bottle to hold hot water.

Solutions Required.

The solutions required for the process are as follows:—

No. 1.—8·75 ounces (250 grms.) caustic soda and 10·7 ounces (300 grms.) caustic potash dissolved in 4 pounds (1809 grms.) water. Use 10 cubic centimetres for each analysis.

No. 2.—Equal parts of commercial sulphuric and acetic acids. The acetic acid should be of 1·047 specific gravity. Use 10 cubic centimetres of the mixed acids for each analysis.

Directions for Analysis.

Taking Samples.—Mix the milk thoroughly by pouring from one vessel to another, avoiding as much as possible the formation of air bubbles; warming the milk to 80° or 90° Fahrenheit will prevent frothing to a large extent. After mixing allow the milk to stand one or two minutes to permit the air bubbles to escape before taking samples. Fill the 20 cubic centimetre pipette by placing the lower end in the milk and sucking until the milk rises in the tube above the mark on the side. Place the finger quickly on the top of the tube and allow the milk to run out slowly until it falls to the mark on the side of the tube; then let the contents of the pipette run into one of the analytical tubes, blowing out the last few drops.

Adding the Alkali.—Fill one of the 10 cubic centimetre pipettes to the mark on the side with alkali, and allow the solution to flow into the milk just measured. Place the finger on the top of the tube and shake the tube until the milk and alkali are well mixed. A rubber cot on the finger will protect it from the action of the alkali. Treat all samples in the same way. Place the tubes in the rack, set the rack and tubes in the water-bath, and heat the bath until the water boils: continue boiling for two hours, or until the contents of the tube become homogeneous and of a dark brown colour similar to that of sorghum molasses. After the tubes have boiled for one hour remove the rack and tubes from the bath and examine the tubes to see if the contents are well mixed. If a whitish layer of casein and fat is found floating on the surface of the liquid, gently shake and roll the tubes until the contents are well mixed. Return tubes to water-bath and boil one hour. The tubes are then ready for the addition of the acid.

Adding the Acid.—Remove the rack with the tubes from the water and allow them to cool to about 150° Fahrenheit. Then, by means of the pipette add 10 cubic centimetres of the acid mixture to each tube slowly, so as not to cause the contents of the tube to froth over. Mix the acid with the contents by running a small glass tube to the bottom of the mixture and blowing gently. Place the rack and tubes again in the bath and heat to boiling for one hour. Remove the tubes from the water, and then, by means of the water-bottle, fill the tubes with *hot* water to within 1 inch of the top. The fat will then rise to the top of the water. Replace the tubes in the bath and allow them to stand in the hot water, without boiling, for one hour. At the end of this time remove the tubes from the bath, one at a time, and measure while hot.

Measuring the Fat.—The analyst will observe that the lines representing the upper and lower limits of the column of fat do not extend straight across the tubes, but are slightly curved. In measuring the column of fat place the rule on the tube so that the lower line will come opposite the lowest part of the curved line of the fat; then read up the scale to the division coming opposite the lowest part of the upper curved line. The number of divisions on the rule is the length of the column of fat in millimetres. The per cent of fat in the milk is then calculated from the following formula and data:—

Amount of milk taken, 20 c.c.
Specific gravity of milk, 1·032.
Specific gravity of insoluble fatty acids, 0·914.
Per cent of insoluble fatty acids in butter fat, 87.

From the above data we have the following formula:—

$$100\,\frac{a\times b\times c}{d\times e}=x.$$

Where a = the length of the column of fat in m.m.
b = the value of one linear m.m. of measured fat expressed in c.c. The value of b will vary according to the size of the tube used.
c = specific gravity of the insoluble fatty acids.
d = 20·64 grms. or the volume of milk taken for analysis multiplied by its specific gravity.
e = per cent of fat present in sample of milk taken for analysis.

Substituting the figures obtained by an actual analysis, the formula would be—

$$100\,\frac{30\times 0{\cdot}027\times 0{\cdot}914}{20{\cdot}64\times 0{\cdot}87}=x=4{\cdot}12$$

per cent of fat in sample of milk analysed.

(Note.—The neck of the tubes can be graduated in c.c., removing the necessity of the troublesome measurements mentioned above.—H. W. W.).

If the process has been conducted according to the above directions the column of fat will be free from impurities, and the line of separation between the water and fat will be perfectly clear. On first rising to the surface the fat is slightly turbid owing to the presence of a small quantity of water. Although this will make no appreciable difference in the measurement of the fat, it may, if desired, be obtained perfectly clear by removing the tubes from the bath and allowing them to cool slowly. The crystallisation of the fat causes the finely divided water, which is distributed through the fat, to collect in drops, which sink to the bottom when the tubes are again heated, leaving the fat perfectly clear.

The analyst may fail to obtain correct results from the following causes:—Either the column of the fat may contain flecks of undecomposed casein, which would increase the volume of fat, thereby giving too high a per cent, or a small quantity of butter fat may remain unsaponified, which will also give too high results. These errors are both caused by insufficient heating of the milk with the alkali, and may be easily obviated by taking care to heat the mixture of milk and alkali for two hours at least. If not pressed for time it is better to heat two and a half hours, and thereby remove all risks of the above errors. If milk containing more than 6 per cent is to be tested, the mixture of milk and alkali should be heated at least three hours. In such case it would be better perhaps to take 10 c.c. in place of the usual amount.

Before adding acid the tubes and contents must be allowed to cool to 150° Fahrenheit at least. If added at a higher temperature the contact of the strong acid with the hot alkali solution will generate sufficient heat to cause the contents of the tube to boil with explosive violence, throwing out the contents of the tube and spoiling the analysis. If after the addition of hot water the tubes are allowed to stand in boiling water, small bubbles of gas are given off by the continued action of the acid on the casein. These bubbles rise through the column of fat, rendering it turbid and causing difficulty in measuring. The bottles containing the solutions of acid and alkali should be kept corked when not in use. If the acid bottle be left open the acetic acid will evaporate and the acid will not dissolve the casein. The alkali bottle should be kept closed to prevent absorption of carbonic acid and consequent weakening of the solution.

(Note.—The method of Short has been compared in my laboratory with the anhydrous copper method of Piggott and Morse. A mean of 12 determinations gave by the anhydrous copper method 3·20 per cent of fat, and by the Short method method 3·18 fat. The same samples treated by the Adams method gave results considerably higher. The process of Short has also been

improved by graduating the neck of the tube into tenths of a c.c.

For use at stations where expensive chemical apparatus cannot be had, the method appears to have great value.—H. W. W.).

Bicarbonate of Sodium in Milk.

Proust makes an energetic protest against the addition of bicarbonate of sodium to milk for the purpose of preserving it. His principal objection to the use of the above salt is based upon its action on lactic acid, the lactate of soda being a salt injurious to children.—(Abstract from *Chemisches Central-Blatt*, No. 24, 1888, p. 837).

(To be continued).

NOTICES OF BOOKS.

Pictures in Black and White; or, Photographers Photographed. By George Mason (Mark Oute). London: Greenwood and Co.

Here is a book which carries the reader back to the time before photography was enlisted in the service of astronomical and biological research, and when it was confined almost exclusively to taking portraits. The author places before us the village fair with its travelling *ateliers*, got up in the style of the showman's caravan, where the curious rustic, half suspicious of necromancy, was invited to have his likeness taken on glass. Not a few of the operators, it must be admitted, were ex-showmen, innocent of physics and chemistry, as of art, who saw in the new invention an easy way of filling their pockets. Nor were they mistaken, for imperfect as might be their results, the public was satisfied and paid cheerfully prices which would now be considered exorbitant.

The careers of these itinerant photographers have been widely different; some of them not content with the little empirical knowledge which they had at their command, studied the principles and practice of their art, and have gradually developed, if not in their own persons, yet in those of their successors, into the qualified photographers whose studios we encounter in all towns of any pretensions.

Others, in whose veins the showman's blood was predominant, lived on the "lightly come, lightly gone" principle, and spent their money as quickly as it was earned, until their art lost the attractions of novelty, and could be exercised to advantage only by men of special taaining. Some of them accordingly returned to their original callings as mountebanks, cheap jacks, comic singers, and what not. Some remained faithful to the camera, and may still be seen in summer time in the outskirts of Epping Forest and other popular resorts ready to "take" the British public for the small fee of sixpence per head. In the good old times half-a-crown would have been paid ungrudingly. What these poor survivals do in the winter is an unsolved problem, which makes us think that the power of hybernation might be a desirable boon to many of the human race.

This book, though it does not in the least touch upon the history of photography as an art, throws an instructive light upon its early career as a profession.

Basic Slag; its Value as a Fertiliser, together with a Short Account of the Principles of Phosphatic Manuring. By C. M. Aikman, B.Sc., F.R.S.E., F.I.C., F.C.S. Edinburgh: *North British Agriculturist.*

This pamphlet is a reprint of certain articles inserted in the *North British Agriculturist*. The author considers that three constituents only of plant food need engage the attention of the farmer, viz., nitrogen, phosphoric acid, and potash, the other minerals taken up by plants being always present in soils in sufficient proportion. Here Mr. Aikman differs from M. Ville, who holds that lime is also requisite, even in the most calcareous soils. The consumption of basic slag, which it is the author's object to recommend as a source of phosphoric acid, is, so far, much less extensive in Britain than in Germany, where it now reaches six million hundredweights yearly. The author points out that the solubility of basic slag is very much greater than that of natural phosphatic minerals, and that its rapidity of action upon the crop is consequently much greater.

According to varied culture experiments its phosphoric acid is about half as valuable as that in soluble phosphates, and it is best adapted to plants of the leguminous kind. Farmers are especially warned against mixing it with sulphate of ammonia, and in like manner with Peruvian guano, since the free lime which it contains will drive off and waste the ammonia.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences. W. F. Clay, 2, Teviot Place, Edinburgh.

This catalogue has an especial claim on the attention of students, professional men, and scientists generally. It includes many complete sets of journals, of the transactions of learned societies, and of the works issued by publishing clubs. Many of these books are extremely scarce, being out of print, and having been, in the first place, issued to subscribers only. Thus we see here announced a complete set of the Cavendish Society's publications, and a complete set of the *Berichte* of the German Chemical Society, which have never been circulated through the trade. There are also sets of *Liebig's Annalen*, of the *Journal of the Chemical Society*, of the *Reports of the British Association*, and of the *Proceedings of the Royal Society*, and many other series valuable for reference.

A few errors in printing are to be met with which may occasionally puzzle the reader. Thus there is here mention of a "Short Text-book of *Morganic* Chemistry," by Prof. Kolbe, a branch of the science which some compositor has evidently evolved out of the depths of his own consciousness.

This catalogue is calculated to be of service to many who are in search of rare or curious scientific works.

CORRESPONDENCE.

WATER ANALYSIS.

To the Editor of the Chemical News.

Sir,—My book on Water Analysis has reached a seventh edition, and entered on its twenty-first year. The widespread and enduring acceptance of the book throws responsibility on its author which he fully recognises.

In sending forth the new edition, the question as to how far modifications and extensions were called for has been very carefully considered.

That portion of the book which deals with the pollution of water by organic matters has not been changed in any way. The second and third sections of the book have, however, undergone alteration and enlargement.

The natural history of water—apart from all considerations of pollution by human intervention—is very interesting, and falls within the scope of the book on water analysis.

The close of part III. is occupied with a sketch entitled "The Classification of Natural Water." Beginning as invisible vapour in the atmosphere water condenses and assumes the liquid or the solid form, and falls to the ground.

It afterwards either sinks into the ground and becomes spring-water, or it remains surface-water. In virtue of its powers of solution it records its own history in its contents, and natural waters possess an identity which they retain until they are evaporated or merged in the ocean.

In former editions reference has been made to the specific gravity of drinking-water. In the present edition is published a research into the specific gravity of drinking-waters, and for the first time a real connection between the contents of an ordinary drinking-water and its specific gravity is established.

The question of the solution of lead by certain kinds of water is also discussed.—I am, &c.,

J. Alfred Wanklyn.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cvii., No. 25, December 17, 1888.

On Certain New Properties of Ethyl Fluoride and on its Analysis.—H. Moissan.—This compound can be prepared in a state of purity by the reaction of ethyl iodide and anhydrous silver fluoride. If heated for several hours to dull redness in a glass bell it yields a complex mixture of carbides containing mere traces of silicon fluoride. Under the action of a weak induction spark it expands greatly, yielding hydrofluoric acid, a small quantity of acetylene, and especially ethylene, without any deposit of carbon. The action of ethyl fluoride upon animals is different from that of ethyl chloride. It produces at first, not anæsthesia, but excitement quickly followed by death.

Compounds of Nitric Oxide with Chloro-ruthenites and the Atomic Weight of Ruthenium.—A. Joly.—The salts described by Claus are not chloro-ruthenites, and compounds of the type $RCl_4,nMCl$ are hitherto unknown both in the case of ruthenium and rhodium. From his numerous and concordant analyses the author deduces for ruthenium the atomic weight 101·5. He adds that the determination of the vapour density, which he previously undertook in concert with H. Debray, leads to an atomic weight lower than 102.

The Use of Hydrogen Peroxide for the Determination of Metals of the Iron Group: (1) Chrome; (2) Manganese; (3) Iron.—Ad. Carnot.—This paper will be inserted in full.

Reproduction of Zircons.— MM. Hautefeuille and Perrey.—Zircons may be obtained at a temperature not exceeding 700° by the action of lithium dimolybdate upon a mixture of zirconia and silica.

Action of Mercury Cyanide upon the Salts of Copper.—Raoul Varet.—Mercury cyanide is not decomposed by the oxy-salts of copper, but by the haloid salts. There is then, as with the alkaline cyanides, an escape of cyanogen, and a formation of cuprous cyanide, which enters into combination with the mercury salt just formed. With the cuprous salts the result is the same, but there is no escape of cyanogen.

On a Diquinolic Base.—Albert Colson.—The base in question is a white solid, of a cotton-like appearance, sparingly soluble in water, soluble in six times its weight of dilute hydrochloric acid, and in ten parts of alcohol at 92°. It is deposited from its solution in ether in the form of long, flattened needles, strongly double refractory. It turns green with concentrated ferric chloride and forms a yellow chloroplatinate and chloraurate; its composition is $C_{22}H_{18}N_2O_3$.

The Combustion-heats of the Camphors and the Borneols.— W. Louguinine.— This memoir does not admit of useful abstraction.

Moniteur Scientifique, Quesneville. Series 4, Vol. ii., September, 1888.

Researches on Porcelain.—Ch. Lauth and G. Dutailly.—The completion of a series of valuable papers, too extensive for reproduction.

Researches on Allo-Isomerism.—A. Michael.—Translated from the *American Chemical Journal.*

On Portland Cement.—Charles Spackman.—From the *Journal of the Society of Chemical Industry.*

The Distinction to be Established between the Mono- and Di-refractive Bodies having a Rotatory Power.—Dr. G. Quesneville.—This purely mathematical paper requires the accompanying diagrams.

Contributions to the Theory of the Vitriol Chambers.—G. Lunge.—From the Chemical News.

Detection and Determination of Selenium in Meteoric Iron.—Mr. Warren.—From the Chemical News.

Academy of Medicine.—Session of July 17th, 1888.—A report on new procedures in vinification proposed as substitutes for "plastering." The conclusions reached are that the introduction into the must of calcium phosphate or of calcium tartrate is open to no objections. Both increase the proportion of the tonic and ferruginous matters, and are besides useful in impeding the formation of the higher alcohols.

The Analysis of Butters and the Determination of the Soluble Fatty Acids.—V. Planchon.—The author proposes a method founded on the following principle:—If we saponify a known weight of fatty matter with a known excess of alkali we may, on neutralising the mixture with a standard acid, determine the proportion of alkali which has combined with the fatty acids. The figure thus obtained called in Germany "Kœttsdorfer's number" has a relation to the quantity of glycerin originally combined and displaced by the alkali. If in place of ceasing to add the standard acid at the moment when neutrality is reached, we continue to drop in this acid so as to employ exactly the quantity corresponding to the alkali which has served for saponification, the soap will be decomposed and the fatty acids will float on the surface. The acids thus isolated may be completely insoluble. In this case, the liquid separated by filtration after cooling will be neutral. If, on the contrary, a portion of the acids is soluble, it will impart to the filtrate an acidity which may be easily estimated by means of a standard alkali. For this process the following solutions are necessary:—1. Semi-normal sulphuric acid very exactly titrated. 2. Normal alcoholic solution of caustic soda. It is prepared by dissolving 45 grms. of pure caustic soda in a minimum of hot water and making the solution up to 1 litre with alcohol at 97°. The standard of this solution is fixed by means of sulphuric acid, just mentioned, adding either alcohol, or a stronger alcoholic solution of caustic soda, so that 25 c.c. may correspond exactly to 50 c.c. of the semi-normal sulphuric acid. 3. Quinque-normal aqueous solution of caustic soda. The saponification is effected in ordinary flasks, with rather wide necks, holding 150 c.c. up to the beginning of the neck. Prior to the analysis we place in these flasks 150 c.c. of alcohol at 15 per cent and heat to 50°—55°. When the temperature is steady we mark with a diamond the level of the liquid, which is then thrown away. We then proceed to the actual analysis as follows:—The butter is first melted in the stove at 50° in a glass dish. As soon as the water and the curd are separated we examine if the fatty matter is clear; if so, the quantity necessary for the analysis is taken with a glass tube, drawn out narrow.

If not, the upper stratum is filtered, and the first portions which pass through are taken. The butter should be left in the stove for a very short time only. The flask being tared to a weight of 5 grms. the weight is removed and the melted butter is added from a pipette so as to re-establish the equilibrium. If we let the drops of liquid fall slowly towards the end we easily avoid exceeding the necessary quantity. We then run into the flask 25 c.c. of the normal alcoholic soda, and boil for twenty minutes with an ascending condenser, either on the sand-bath or over a very small gas flame. At the end of this time the saponification is completed; the source of heat is removed, the flask is let cool for some minutes, and about 60 c.c. of distilled water are then added and a few drops of phenyl phthaleine. The semi-normal acid is then run into the soapy solution by means of a burette with a glass cock, holding 50 c.c., and graduated to $\frac{1}{10}$ c.c. When the red tint disappears we read off the quantity of acid used, and note this first result. Without removing the flask we continue the addition of the semi-normal acid until the total volume used is 50 c.c. (or rather, a number bordering on 50 c.c., found necessary in blank experiments for the exact neutralisation of the 25 c.c. of soda). The flask is then set on the water-bath, heated to 50°—55°, when the insoluble fatty acids melt and separate. The flask is repeatedly agitated, and when the temperature is steady we add a quantity of luke-warm distilled water sufficient to raise the *lower* level of the stratum of fatty acids to the mark at the bottom of the neck. The flask is then closed with the finger and well shaken so as to break up the acids, and it is then left to cool. When the upper stratum is clear the flask may be set in cold water, when the fatty acids crystallise. When completely cold we filter and take, of the filtrate, 100 c.c. for titration with the quinque-normal alkali. We may here stop, as the two indications already obtained permit us to decide on the purity of the sample. But we generally determine also the proportion of the insoluble fatty acids, especially if the presence of margarine is evident. To this end, whilst the fatty acids are cooling we tare accurately a filter without folds, dried at 100°; the solution of the soluble acids is passed through this filter, which retains the small clots carried along with the liquid, and we set aside the first 100 c.c. of the filtrate for titration. The cake of fatty acids remaining in the flask is taken up with boiling water; its melting-point is determined, and the whole is poured into the tared filter. A few washings with boiling water suffice to cleanse the flask and to free the filter from sodium sulphate. The funnel and its contents are placed in cold water and after the crystallisation of the fatty acids the filter is placed in a tared platinum capsule set in a Gay-Lussac stove. The first weighing is effected after three hours of desiccation, and the further loss is verified from hour to hour. In case of pure butter the loss does not fall to 5—6 m.grms. per hour until after 6—7 hours. The operation is then stopped and the final weight taken.

Industrial Review, and Patents Taken.—A collection of specifications chiefly German and English.

New Process for the Volumetric Determination of Sulphates in Presence of other Salts.—D. Sidersky.—This method will be inserted in full.

October, 1888.

Chemical Action of Certain Micro-organisms.—R. Warington.—From the *Journal of the Chemical Society*.

Action of the Aldehyds upon the Phenols.—H. Causse.—In this paper the author studies the action of glyoxylic acid, ethylic aldehyd, of heat, of zinc-powder, potassa, acetic anhydride, and acetone upon resorcine.

Manufacture of Explosives by Nobel's Explosives Company.—From the *Journal of the Society of Chemical Industry*.

The Oxidation of Linseed Oil Considered as an Analytical Procedure.—A. Chenevier.—The author considers that the oxidation method proposed by M. Livache may constitute an industrial procedure capable, in certain cases, of superseding the boiling oils with litharge. It may also furnish indications on the drying quality of any oil by an observation of the time which it requires, when once prepared, to dry upon a plate of glass. We have thus the advantage of knowing the drying properties of the oil, independently of substances which may be mixed with it afterwards. But it is inaccurate to rely upon the increase of weight of the oil, for it is too variable according to circumstances which are independent of its quality. For a linseed oil the best index of quality is still the specific gravity. The higher the gravity of an oil the better it dries. This is the difference between oils from French and from foreign seeds (Bombay, Calcutta, La Plata, &c.) The specific gravity of the former is always at least 0·9325, whilst the oils from foreign seeds are often below 0·932.

Influence of the Composition of Glass upon the Slow Displacement of the Zero in Thermometers.—R. Weber.—From the *Journal of the Chemical Society*. (*Berichte*, xxi., 1086).

Synthetic Formation of Closed Chains of Carbon.—MM. Colman and Perkin.—From the *Journal of the Chemical Society*.

The Production of Indigo in China.—From the *Journal of the Society of Arts*.

Ultramarine by the Moist Way.—Dr. F. Knapp.—The author has examined the preparation of ultramarine with silica alone, with alumina alone, or blue of the ultramarine type prepared with sodium salts or with calcium phosphate, the sodium sulphide, and the black precipitate extracted from it, and black sulphur, which he considers identical with the black sulphur of Magnus. In preparing ultramarine by the dry way sodium carbonate is added to the clay and the sulphur. Potassium carbonate cannot be used either in the dry or the wet process. There is no analogy between the two alkalies as regards the special properties of their sulphides. The sulphide obtained by fusing potassium carbonate with an excess of sulphur is devoid of that green shade observed in the corresponding sodium compound, but is of a pure reddish brown. If dissolved in water it deposits no black matter, and the solution is never green, but reddish brown.

The Origin and the Transformations of Nitric Acid in Plants.—From the *Journal of the Chemical Society*, but originally abstracted from the *Proceedings of the German Botanical Society*.

The Azo-colours.—Paul Richard.—An important paper not capable of being compressed within our limits.

Determination of Nitrotoluene in Ortho- and Para-nitrotoluene.—MM. Reverdin and De la Harpe.—The process is based upon the fact that sulphonised para-nitrotoluene is easily transformed by boiling with soda into a stilbene derivative (dinitrodisulphostilbene), the strongly alkaline solution of which has a deep red colour, whilst the corresponding ortho-compound is not attacked under the same conditions, and its alkaline solution remains colourless. The authors dissolve in fuming sulphuric acid orthonitrotoluene containing a known proportion of paranitrotoluene, say 5 per cent. They heat slightly in the water-bath, and when the sulphonation is complete they pour the solution into water, neutralise with soda, and dilute with much water, so that 1 c.c. of the solution, if heated with a given and unvarying quantity of a solution of caustic soda, takes a pale rose shade. They then operate in the same manner with the sample under examination, and dilute progressively the neutralised solution until 1 c.c. of this solution heated with soda gives the same shade as the type. The volume of this solution, compared with that of the type, is directly proportional to the quantity of para in the sample.

The Reduction-products of Hematoxyline. — J. Hegler.—The author has reduced the acetylic derivative of hæmatoxylene by means of zinc-powder. The product which passes over below 300° is a yellow solid, soluble in alcohol, ether, glacial acetic acid, and benzol, from which it crystallises in small yellow needles. Below 300°, and chiefly between 250° and 260°, there passes over a yellow oil, of a strong odour and insoluble in alkalies.

The Contact of Carbon and Other Substances at High Temperatures and under Strong Pressures.—Ch. A. Parsons.—From the CHEMICAL NEWS.

MISCELLANEOUS.

The Late Professor Tuson.— The friends of the late Professor Tuson find, with deep regret, that his death, at the premature age of 56, leaves his widow, with two daughters in delicate health dependent on her, entirely unprovided for. The undermentioned have kindly consented to act as a Committee for the purpose of raising a fund for her benefit, and it is hoped that a sufficient sum may be subscribed to enable them to purchase an Annuity or make some other suitable provision for her. The Honorary Secretaries will be very pleased to receive the names of any other gentlemen who may be willing to join the Committee, and most earnestly solicit subscriptions to the fund. Any amounts forwarded to Richard A. N. Powys, Esq., Royal Veterinary College, Camden Town, N.W., will be duly acknowledged. Subscriptions may also be paid to Messrs. Herries, Farquhar, and Co., 16, St. James's Street, S.W., to the credit of the "Tuson Fund." *Committee.*—Sir F. A. Abel, C.B., F.R.S., Prof. Attfield, F.R.S., Prof. Axe, M.R.C.V.S., E. Bellamy, F.R.C.S., Prof. Bernays, F.I.C., F.C.S., Prof. Brown, C.B., Hon. Associate R.C.V.S., Lloyd Bullock, F.C.S., Michael Carteighe, F.I.C , F.C.S., Spencer Chapman, Edward Clark, William Crookes, P.C.S., F.R.S., Warren, De la Rue, D.C.L., F.R S., H. Favarger, Dr. J. H. Gladstone, F.R.S., H. A. Greig, G. Harley, M.D., F.R.S., C. W. Heaton, F.I.C., F.C.S., F. J. Honey, A. H. Hooker, F.I.C., F.C.S., David Howard, J.P., F.C.S., C. R. Lightbody, Dr. Rudolph Messel, A. F. Moens, L. Mond, F.I.C., F.C.S., Hugo Müller, F.R.S., G. Plater, Prof. Penberthy, F.R.C.V.S., Richard A. N. Powys, Prof. Pritchard, F.R.C.V.S., W. O. Robinson, Prof. Shave, M.R.C.V.S., Prof. Simonds, Hon. Associate R.C.V.S., Harold Simpson, S. Harman Sturgis, John Spiller, F.I.C., F.C.S., W. Walker, and F. Wragg, F.R.C.V.S. *Hon. Secretaries*—C. W. Heaton and Richard A. N. Powys.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Medical, 8.30.
— Society of Chemical Industry, 8. "Notes on Explosives," by C. Napier Hake.
TUESDAY, 8th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Royal Institution, 3. "Clouds and Cloudland," by Professor Dewar, M.A., F.R.S.
WEDNESDAY, 9th.—Geological, 8.
— Microscopical, 8.
— Pharmaceutical, 8.
THURSDAY, 10th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
FRIDAY, 11th.—Astronomical, 8.
— Quekett Club.

NOTES AND QUERIES.

***** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.**

Science and Art Department.—(Reply to "Student.")—The querist will find what he requires on p. 73 of Jarmain's "Qualitative Analysis" (fifth edition), and also on page 238 of Valentin's "Qualitative Analysis" (sixth edition, 1884). The latter does not include salicylic acid, but this could be specially tested for.—YOUNG ANALYST.

ST. PAUL'S SCHOOL.—An Examination for filling up about Eight Vacancies on the Foundation will be held on the 16th January next.—For information apply to the Bursar, St. Paul's School, West Kensington.

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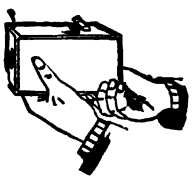

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London: Printed and Published for the Proprietor by EDWIN JOHN DAVEY, at the Office, Boy Court, Ludgate Hill, E.C.

THE CHEMICAL NEWS.

Vol. LIX. No. 1520.

THE RAPID AND SURE DETECTION OF ANTIMONY IN MINERALS.*

By ALEXANDER JOHNSTONE.

(Additional Note).

By adding a drop of ammonium sulphide to the white incrustation of Sb_2O_3 obtained by heating the antimoniferous mineral with fusion mixture in the inner blowpipe flame, I have shown how antimony can be rapidly and surely detected. When the antimony is present in *very* small quantity, the charcoal method must be the one adopted. In other cases, however, when the metal is more abundant, it can be quickly and very satisfactorily identified by heating the substance, with the addition of fusion mixture, in a glass tube (having about ¼" bore) *open at both ends*. A little of the mixture of pounded mineral and flux is placed in a glass tube at a distance of about a quarter of an inch from the end. The tube is inclined slightly, and heat by means of a blowpipe flame is applied. Dense white smoke is produced, and a white sublimate deposits on the upper and sometimes also on the lower side of the tube. Touch this white sublimate with a *single* drop of ammonium sulphide, and at once the highly characteristic orange sulphide of antimony is produced very distinctly. No other white sublimate obtained in the open tube in the manner described than Sb_2O_3 is converted into an orange-coloured substance on the application of ammonium sulphide.

Edinburgh University.

ON THE COLOURATION OF A COAL FIRE BY COMMON SALT.

By NORMAN LEONARD, B.Sc.

It is probable that many readers of the Chemical News have, like myself, been questioned as to the cause of the blue flame produced when a pinch of ordinary table salt is thrown into a coal fire. I have, however, never met with anyone who could explain the phenomenon, which appears to contradict the results of the usual experiments on flame colourations, in which a spirit or gas-lamp is used. Among the attempts at explanation which I have heard suggested are:—(1) That the vapours arising from the salt prevent complete combustion, the blue flame of carbon monoxide being the result. (2) That the sodium flame cuts off the yellow light emitted by the glowing coals, and only allows the red and blue to pass. (3) That the colouration is due to the chlorine of the salt, which may perhaps combine with the carbon and hydrogen of the fuel to form compounds, such as chloroform and tetrachloride of carbon, which are, in their turn, decomposed and oxidised, with production of the colouration in question.

The blue colouration seems to me to be of too purple a shade to admit of the truth of the first theory. The second theory seems rather far-fetched, but the third is pretty well borne out by the following facts, the result of some experiments which I have recently made.

1. The blue flame is not produced when sodium chloride is projected on to a red-hot platinum capsule.

2. The colouration produced by throwing sodium chloride into a coal fire is produced equally well by potassium chloride and less readily by the chlorides of barium, calcium, and ammonium.

3. The colouration is not produced by the carbonate, phosphate, or sulphate of sodium.

4. Chloroform, carbon tetrachloride, and ethylene dichloride, when thrown into a coal fire, produce blue colourations, similar to that produced by sodium chloride.

THE USE OF HYDROGEN PEROXIDE FOR THE DETERMINATION OF METALS OF THE IRON GROUP: (1) CHROME; (2) MANGANESE; (3) IRON.

By ADOLPH CARNOT.

(1) *Chrome.*—The author has shown that oxygenated water rapidly and completely reduces chromic acid in a cold acid solution. In a hot alkaline or ammoniacal solution it effects the inverse transformation, and may be used for entirely peroxidising chromic oxide. The reaction presents a peculiar interest in an ammoniacal solution, differing from all the methods employed for the peroxidation of chrome, in as far as it dispenses with the use of fixed reagents, which are always undesirable in analyses.

A dilute solution, *e.g.*, of chromium chloride, heated to 100° with the addition of a few c.c. of oxygenated water, then supersaturated with ammonia and heated anew to ebullition, becomes at first brown and turbid, then clear and pale yellow, passing to the state of ammonium chromate. The reaction is promoted by agitation, during which there is an escape of oxygen. If there remains a little chromium oxide not transformed, it must be let settle, separated by decantation, re-dissolved in an acid, and again treated with oxygenated water and ammonia.

When the peroxidation is complete the chromic acid may be determined volumetrically either with hydrogen peroxide or some other reducing agent in a standard solution. It is merely necessary for this determination that no trace of the first reagent may remain. But this is an easy precaution, as the hydrogen peroxide disappears completely after a few minutes' boiling in presence of a sufficient excess of ammonia. There is also sufficient indication of its presence, for on acidifying the cold liquid we see appear the blue tint characteristic of hydrogen peroxide in presence of chromic acid. It should then be boiled again with ammonia and a little hydrogen peroxide. The same reagent may also be used in gravimetric analyses, but its purity must be first ascertained. The presence of hydrochloric or sulphuric acid does not in general occasion any inconvenience.

Chrome may be thus peroxidised in an ammoniacal liquid and separated in one or two such operations from oxides which are precipitated by ammonia or ammonium carbonate. The solution of chromate can then be reduced by hydrogen peroxide in presence of a slight excess of acid, and heated to boiling. If we supersaturate with ammonia there will be partial peroxidation of the chrome by any peroxide of hydrogen which has not been destroyed, and the liquid will remain yellow. To avoid this inconvenience a current of sulphuretted hydrogen is passed for a few moments into the hot liquid, saturating it then with ammonia and letting it boil. The precipitation of the oxide of chrome is thus quite complete.

Chrome may be also determined very well by adding to the slightly acid solution, just reduced with hydrogen peroxide, first phosphate and then sodium or ammonium acetate, and boiling for ten to fifteen minutes. As the liquid remains acid, there is no peroxidation, and we obtain the precipitate of hydrated chromium phosphate of a fine green.

These two methods, volumetric and gravimetric,

* See Chemical News, vol. lviii., p. 296.

furnish simple solutions for various problems of chemical analysis. If, *e.g.*, we wish to determine the proportions of chromic acid and of chromium sesquioxide in a mixture, the chromic acid is determined volumetrically with oxygenated water, and the total chrome is then precipitated as oxide or phosphate.

If we have a mixture of alkaline chromate and aluminate, like that found after chrome iron has been attacked with an alkaline flux and the silica has been separated, we determine the chromic acid with oxygenated water and then precipitate together and weigh the chromium and aluminium phosphates; knowing the chromium, the aluminium is calculated as the difference. If we have a solution containing iron and chrome as sesquioxide, we peroxidise with hydrogen peroxide and ammonia, boiling for five to ten minutes. We then re-dissolve in a slight excess of acid and determine the chromic acid and ferric oxide as indicated for alumina in the previous case.

(2) *Manganese.*—In an acid liquid manganese, like chrome, is reduced by hydrogen peroxide, and in an ammoniacal solution it is peroxidised. We need not enlarge on the former reaction, which is well known and is utilised in the determination of oxygenated water with potassium permanganate. The second reaction may claim some attention on account of the facility which it offers for the determination of manganese. If we pour a few c.c. of oxygenated water and afterwards ammonia into a solution containing a manganous salt, there is at once produced a dark brown precipitate containing the total manganese. On heating to a boil the precipitate collects together, but it retains a portion of the bases which existed in the liquid, and which can only be removed by a series of similar precipitations, which may, however, be executed very rapidly. The volumetric determination can always be effected satisfactorily. The author has ascertained that the manganese is entirely precipitated as peroxide, whether it exists alone or along with lime, baryta, oxide of zinc, or ferric oxide. The solution is made ammoniacal and boiled for about ten minutes in order completely to remove any excess of hydrogen peroxide. The oxygen of the peroxide, and consequently the manganese itself, is determined volumetrically; for instance, by means of oxalic acid, sulphuric acid, and potassium permanganate.

(3) *Iron.*—It is well known that iron, unlike the two former metals, is peroxidised by hydrogen peroxide in an acid solution. The conversion is immediate, even in the cold, and is effected more easily than with any other oxidising agent.—*Comptes Rendus*, vol. cvii., p. 997.

SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,
Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

(Continued from p. 7).

The IIIrd group of the cadmium-rays embraces the rays observed principally by Hartley and Adeney.

λ =		
*4414·5		nodal rays of the IIIrd and IVth group.
*4115·2		
*3986·0	Mascart	
3976·3		
3974·5		
3940·0		
3851·0		
3810·0		
3682·6 (?)		of doubtful origin, like an impurity, as it proceeds from one electrode only.
3611·8	strong.	
3609·6	very strong.	
3608·0	Mascart.	
3535·0		
3466·8	strong.	
3465·4	very strong.	
3402·9	very strong.	
3384·7		
3288·0	Mascart.	
**3233·6	nodal ray of the IIIrd and Vth group.	

The wave-lengths λ of these rays belong to the group (H, *b*), or to that condensation form of the primary body "*b*" in which it occurs in free hydrogen, and (besides other condensation forms) also in the vapour of magnesium and of carbon.

They satisfy, indeed, according to the Tables III, III*a*, III*b*, and III*c*, more or less completely the known criteria of such rays, which I have already mentioned in the discussion of the IInd group, and given for the wave-lengths (λ′) there occurring.

They can be summarily expressed by the following symbolic equations:—

$\frac{1}{1}$ (H, *b*) = (H_2O, H, *b*) water spectrum (first chief criterion).

$\frac{1}{1}\frac{1}{1}$ · $\frac{1}{1}\frac{1}{1}$ (H, *b*) = (H_2O, O, O′, *b*) water spectrum (second criterion).

$\frac{1}{2}\frac{1}{1}$ · $\frac{1}{3}\frac{0}{0}$ (H, *b*) = (H_2O, O, O′, O″, *b*) water spectrum (third criterion).

$\frac{2}{3}$ (H, *b*) = (H_2O, H) water spectrum (fourth criterion).

and—

$\frac{1}{1}\frac{1}{1}$ (H, *b*) = (O, O′ *b*) oxygen (first accessory criterion).

$\frac{1}{3}\frac{1}{0}$ (H, *b*) = (O, O′, O″, *b*) oxygen (second accessory criterion).

The wave-lengths λ, in the first column of the tables, which satisfy simultaneously the seven criteria with great accuracy, proving thereby the existence of this group.

The rays λ = 4414·5, 4115·2, 3986, connect the IIIrd and IVth, the ray 3233·6 the IIIrd and Vth group as nodal rays.

"Cadmium contains, therefore, the primary body "*b*" in the same chemical state as in free hydrogen, but in another physical modification."

The IVth group of the cadmium-rays is composed of the following rays:—

λ =		
*5337·0	very strong, Kirchhoff	empirical nodal rays of the IIIrd and IVth.
*5153·0	Huggins	
4798·0	strong, Huggins.	
4677·6	+Liveing and Dewar.	
4676·7	Hartley and Adeney.	
4416·0	Huggins (4415·5, strong, Thalén).	
**4414·5	Hartley and Adeney, nodal ray of the IIIrd and IVth group.	
4215·3	Hartley and Adeney.	
4158·0 (?)	,, ,,	
4141·0	,, ,,	
4127·4	,, ,,	
**4115·2	,, ,,	nodal ray of the IIIrd and IVth group.
3987·6	,, ,,	
**3986·0	Mascart, nodal ray of the IIIrd and IVth group.	
3498·2	Hartley and Adeney.	

The cited rays are "*c*" rays, due to the primary body "*c*" in the same chemical state as in free oxygen or in magnesium vapour. For the wave-lengths λ give (see Table IV.), by multiplication with $\frac{1}{1}$, $\frac{1}{1}$, and $\frac{1}{3}$, corresponding wave-lengths, $\frac{1}{1}$λ, $\frac{1}{1}$λ, $\frac{1}{3}$λ of the water spectrum, and answer thereby to the known criteria of the "*c*" rays, which can be shortly expressed by the following symbolical equations:—

$\frac{1}{1}$ (*c*) = (H_2O, O, O′, O″, *c*) (first or chief criterion).

$\frac{1}{1}$ (*c*) = (H_2O, O, O′, O″) (second criterion).

$\frac{1}{3}$ (*c*) = (H_2O, O) (third criterion).

The physical modification in which "*c*" occurs in cadmium seems to be similar to that in which it occurs

* A Paper read before the Royal Society, December 13, 1888.

in oxygen; as several "*c*" rays of cadmium, viz., λ = 4476·7, 4416, 4414·5, and 4158·0 (?) agree almost completely with corresponding "*c*" rays of oxygen.

The group under discussion is connected with the IInd group by the nodal rays λ = 5337, 5153, and with the IIIrd group by the nodal rays λ = 4414·5, 4115·2, and 3986. The wave-lengths λ of those rays, which satisfy all three criteria, and are therefore characteristic of this group. Cadmium contains consequently the primary body "*c*" also in the same chemical state as in oxygen or in magnesium, and in physical modifications similar to that of the "*c*" in oxygen.

The Vth group of the cadmium-rays (see the Tables V., V.*a*, V.*b*, V.*c*), is a very numerous one. Their wave-lengths are, according to Hartley and Adeney (st. = strong, v. st. = very strong, f. st. = fairly strong)—

λ =	
3285·3	
3282·9	
3276·4	
3264·1	nebulous.
3260·2	st.
3251·8	
3249·5	st.
*3233·6	empir. nodal ray of the Vth and IIIrd group.
3222·6	
3219·9	
3216·0	
3211·8	
3200·6	
3196·8	
3194·9	
3185·1	st.
3181·5	
3176·1	(?)
3172·9	st.
3161·0	st.
3156·6	
3152·7	
3132·5	
3129·4	st.
3123·6	
3120·9	
3117·8	f. st.
3112·0	
3095·0	st.
3090·5	
3087·7	
3084·3	st.
3080·2	
3076·7	
3073·2	
3067·8	f. st.
3064·0	st.
3058·4	f. st.
3052·3	f. st.
3048·2	f. st.
3034·9	
3023·8	
3016·1	
3013·8	
3002·2	
2994·8	
**2986·1	empir. nodal ray of the Vth and VIth group.
2979·9	st.
2970·2	
**2964·5	empir. nodal ray of the Vth and VIth group.
2951·4	
2947·1	f. st.
**2909·9	empir. nodal ray of the Vth and VIth group.
2880·1	st.
**2868·0	empir. nodal ray of the Vth and VIth group.
2833·0	
2832·3	
**2807·3	empir. nodal ray of the Vth and VIth group.
λ =	
**2804·0	empir. nodal ray of the Vth and VIth group.
2774·5	
2766·5	
**2763·1	empir. nodal ray of the Vth and VIth group.
**2726·9	empir. nodal ray of the Vth and VIth group.
**2706·0	empir. nodal ray of the Vth and VIth group.
**2677·2	empir. nodal ray of the Vth and VIth group.
**2645·4	empir. nodal ray of the Vth and VIth group.
2632·3	
2630·2	
2618·0	
2614·0	
**2611·0	empir. nodal ray of the Vth and VIth group.
2600·8	
**2598·8	empir. nodal ray of the Vth and VIth group.
**2574·2	Mascart, empirical nodal ray of the Vth and VIth group.
**2563·2	empir. nodal ray of the Vth and VIth group.
2551·6	
**2547·2	empir. nodal ray of the Vth and VIth group.
2499·6	
**2488·2	empir. nodal ray of the Vth and VIth group.
**2469·3	f. st.; empir. nodal ray of the Vth and VIth group.
**2376·6	empir. nodal ray of the Vth and VIth group.
2329·5	st.
2313·6	v. st., broad; Hartley.
2313·5	Cornu.
** 2288·9 v. st., broad; 2288·5 Cornu	empir. nodal ray of the Vth and VIth group.
2268·6	
2265·9	v. st., broad.
**2227·0	empir. nodal ray of the Vth and VIth group.
2206·0	
2111·5	

The foregoing numbers agree almost completely with corresponding wave-lengths of the water spectrum. They are transformed by multiplication with the factor $\frac{4}{3}$ into numbers $\lambda' = \frac{4}{3}\lambda$, which possess, unmistakably, the characteristic marks of wave-lengths due to the group (H, *b*).

The wave-lengths λ belong, therefore, to the very large group of wave-lengths (H_2O, H, *b*) which the primary body "*b*" produces in the chemical state in which it exists in the bound hydrogen of aqueous vapour.

The Tables V., V.*a*, V.*b*, V.*c*, which form in reality only one table, but divided into several branches, because the first columns of Tables V.*a*, V.*b*, V.*c*, coincide with the third column of Table V., give us a plain idea of the remarkable relations and agreements which the Vth group shows in regard to the criteria quoted summarily below. The wave-lengths are also here, and in the tables, those which satisfy most completely and exactly the criteria.

Criteria of the Vth Group.

*Cd λ = (H_2O, H, *b*) water spectrum (first chief criterion).

$\lambda' = \frac{4}{3}\lambda$ = (H, *b*) hydrogen (accessory criterion).

$*\frac{8}{33} \cdot \frac{40}{41}\lambda'$ = (H_2O, O, O', *b*) water spectrum (second criterion).

$\frac{40}{41}\lambda'$ = (O, O', *b*) oxygen (accessory criterion).

$*\frac{1}{33} \cdot \frac{10}{33}\lambda'$ = (H_2O, O, O', O'', *b*) water spectrum (third criterion).

$\frac{10}{33}\lambda'$ = (O, O', O'', *b*) oxygen (accessory criterion).

$*\frac{2}{3}\lambda'$ = (H_2O, H) water spectrum (fourth criterion).

Among the rays of the Vth group occur, besides the empirical nodal ray 3233·6 already mentioned in the IIIrd group, a series of rays which satisfy not only the criteria of that group, but also that of the VIth group, being, therefore, empirical nodal rays of the Vth and VIth group.

These rays are—

λ=2986·1 ·, 2964·5 ·, 2909·9 ·, 2868·0, 2807·3 ·, 2804·0 ·, 2763·1, 2726·9 ·, 2706·0 ·, 2677·2, 2645·4—, 2611·0—, 2598·8—, 2574·2, 2563·2—, 2547·2—, 2488·2, 2469·3, 2376·6+, 2288·9, 2227·0—.

The wave-lengths λ=2574·2 (Mascart), 2288·9 (Hartley and Adeney), answer on the photographs to certain points of very broad and strong lines; λ=2469·3 is a fairly strong line. The wave-lengths followed above by short lines or thick points belong, according to Hartley and Adeney, to short relatively to very short lines. The forementioned lines may, for the most part, be only seemingly, and not truly nodal rays; if they be not really nodal rays, they may be either double rays, one of which belongs to the Vth, and the other to the VIth group, or such rays as might be proved, by more accurate measurements of the wave-lengths of Cd, H_2O vapour, and of the other comparison spectra, to belong only to one of the two groups, (thus probably 2807·3, 2726·9, 2488·2, 2376·6, only to the Vth, and 2909·0, 2804·0, 2706·0, 2677·2, 2611·0, 2598·8, 2574·2, 2563·2 only to the VIth group).

The rays of the IIIrd group, λ=3402·9, 3288, and the ray λ=3176·1, belong, according to the criteria, probably also to the Vth group, though they (perhaps from their faintness) have not hitherto been observed amongst the rays of the water spectrum.

"Cadmium contains, in consequence of the above explanation, the primary body "*b*" in that chemical condensation form in which it occurs also in the hydrogen bound in aqueous vapour, being at the same time in a very similar physical state."

Peculiarly related to the structure of cadmium, and therefore of great importance as a point of departure for new researches, which throw an unexpected light upon the structure of the bodies hitherto looked upon as elements (see the Introduction), is the VIth group of the cadmium rays, (Tables VI., VI.*a*, VI.*b*, VI.*c*). It includes the rays observed (with few exceptions) by Hartley and Adeney (st. = strong, v. st. = very strong, f. st. = fairly strong, bd. = broad):—

λ =	
3209·0	
3177·9	
*2986·1	empir. nodal ray of the Vth and VIth group.
*2964·5	empir. nodal ray of the Vth and VIth group.
*2909·9	empir. nodal ray of the Vth and VIth group.
*2868·0	empir. nodal ray of the Vth and VIth group.
2836·1	f. st.
*2832·3	empir. nodal ray of the Vth and VIth group.
*2807·3	empir. nodal ray of the Vth and VIth group.
*2804·0	empir. nodal ray of the Vth and VIth group.
2779·8	
*2763·1	empir. nodal ray of the Vth and VIth group.
2747·7	v. st., bd.
2743·0	Mascart.
*2726·9	empir. nodal ray of the Vth and VIth group.
*2706·0	empir. nodal ray of the Vth and VIth group.
*2677·2	empir. nodal ray of the Vth and VIth group.
2658·5	
2649·4	
2645·4	
2639·7+	
2639·5—	
2635·3	
2632·7	
2629·1	
2624·8	
*2611·0	empir. nodal ray of the Vth and VIth group.
*2598·8	empir. nodal ray of the Vth and VIth group.
2595·3	
2592·0	
2587·8	
2585·0	
2574·2	Mascart; empir. nodal ray of the Vth and VIth group.
2572·2	v. st., bd.
*2563·2	empir. nodal ray of the Vth and VIth group.
2557·4	
2555·0	
*2547·2	empir. nodal ray of the Vth and VIth group.
2544·5	
*2488·2	empir. nodal ray of the Vth and VIth group.
*2469·3	f. st.; empir. nodal ray of the Vth and VIth group.
2418·5	
2377·3	
*2376·6	empir. nodal ray of the Vth and VIth group.
2321·6	v. st.
2321·8	Cornu.
2318·0	Mascart.
2312·5	value of L. Bell's 2312·83 on Rowland's scale reduced to Angstrōm's scale.
2307·0	st.
*2288·9	v. st., bd. } empir. nodal ray of the Vth and
2288·5	Cornu. } VIth group.
2249·2	
2241·4	f. st.
*2227·0	empir. nodal ray of the Vth and VIth group.
2217·1	(?) Mascart.
2196·4	st. bd.
2194·5	Cornu.
2146·8	st., bd.
2144·1	Cornu.

The wave-lengths λ of this group are transformed by multiplication with the factor $\frac{7}{8}$ to wave-lengths $\lambda'=\frac{7}{8}\lambda$ belonging to the group (H_2O, H, *b*), which can be recognised and proved to be such by the known criteria, quoted summarily and used already in the discussion of the Vth group, which forms also a partial group of (H_2O, H, *b*). We have only to write there λ' instead of λ, and λ'' instead of λ', to adapt the criteria formerly used to the present conditions.

The criteria of the VIth group are therefore shortly—

*$\frac{7}{8}$ Cd. λ=(H_2O, H, *b*)λ' water spectrum (first or chief criterion).

$\lambda''=\frac{4}{7}\lambda'$ hydrogen (accessory criterion).

*$\frac{11}{8}\cdot\frac{11}{7}$ λ''=(H_2O, O, O', *b*) water spectrum (second criterion).

$\frac{11}{7}\lambda''$=(O, O', *b*) oxygen (accessory criterion).

*$\frac{11}{8}\cdot\frac{10}{9}$ λ''=(H_2O, O, O', O'', *b*) water spectrum (third criterion).

$\frac{10}{9}\lambda''$=(O, O', O'', *b*) oxygen (accessory criterion).

*$\frac{8}{7}$ λ''=(H_2O, H) water spectrum (fourth criterion).

The reader will find the comparisons prescribed by the above cited criteria, carried out in the Tables VI., VI.*a*, VI.*b*, VI.*c*, the three latter of which are only three different combinations of the first (VI.), as the first columns of VI.*a*, VI.*b*, VI.*c* are identical with the fourth column of VI.

The special arrangement of the single tables is easily understood without further explanation. The figures here also are those which satisfy in the best manner the most part of the given criteria (including the chief criterion), or rather those for which the proofs referred to are the most conclusive with the measurements known at present.

The empirical (and perhaps for the most part only seeming, not real) nodal rays of the Vth and VIth group have already been treated in detail in the discussion of the latter. Finally it may be remarked that the signs + or — annexed at the right hand to several wave-lengths indicate that the true values of them might be, having regard to the criteria, relatively greater or smaller.

With regard to my previously established fundamental theorem (*Astronomische Nachrichten*, 1887, No. 2797), the above discussion shows that cadmium contains the primary body "*b*" also in a chemical state, $\frac{7}{8}$ times more condensed than in the chemical states corresponding to the Vth group, viz., $\frac{7}{8}$ times more condensed than in the bound hydrogen of aqueous vapour.

This condensation form is therefore the strongest of all condensation forms of "*b*" occurring in cadmium; and the primary element "*b*" forms in this chemical state the kernel, upon and around which the other condensation forms of the primary bodies "*b*" and "*c*" have been stored in the original formation of the cadmium. Summing the results of all our former discussions, we can enunciate as the chief result of our spectrum analysis of cadmium the following statement:—

Cadmium is a compound that behaves itself in all chemical processes hitherto known as a radical or relative element.

It contains, according to the analysis of its line spectrum as at present known, the primary element "*b*" of hydrogen ($H = ba_4$) in four, and the primary element "*c*" of oxygen and magnesium in (at least) two different chemical states, viz.:—

I. *The Primary Element* "c."

(α). In the same chemical state as in oxygen, magnesium, and carbon, and in a physical modification similar (partly at least) to that in which it occurs in oxygen; it emits in this state the IVth group of the cadmium rays.

(β). In a state more dilated than the former in the ratio 2:3, producing the Ist group of the cadmium rays.

II. *The Primary Element* "b."

(α). In a chemical state as in "helium," that is to say in the state into which it comes when hydrogen ($= ba_4$) begins to be associated by sufficiently elevated temperature, and perhaps also by simultaneously suitably diminished pressure, expanding itself at once in the ratio 2:3; it emits in this state the IInd group of the cadmium rays.

(β). In the same chemical condensation form as in free hydrogen ($= ba_4$), but in another physical modification, originating the IIIrd group of the Cd rays.

(γ). In the same chemical condensation, and at the same time in a physical modification, very similar to that in which it occurs in the bound hydrogen of aqueous vapour, giving out the rays of the Vth group; finally:

(δ). In a condensation form in which "*b*" is $\frac{1}{2}$ times more condensed than sub (γ), emitting the rays of the VIth group. In this state of relatively maximum condensation it forms the "kernel," upon and around which the other condensation forms of the primary bodies "*b*" and "*c*" have been stored in the original formation of the cadmium under circumstances hitherto entirely unknown.

"The primary substance '*c*' in the state cited sub I. (α), and the three condensation forms of '*b*' quoted sub II. (α), II. (β), and II. (γ), occur also in magnesium (see 'Mathematische Spektralanalyse des Magnesium's und der Kohle,' 1887, in the *Sitzungsberichte der Wiener Academie*), but evidently in less quantity by weight, according to the less atomic weight of magnesium, thus accounting for the near relation existing between cadmium and magnesium."

(To be continued).

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Continued from p. 10).

Butter Analysis.

Action of Alcohol on Butter Fat.

Cochran has made experiments on the solubilities of the different glycerides of butter in alcohol with reference to the quantity of volatile acid which the dissolved and undissolved portions would yield when treated by Reichert's method. As a result of the work it is seen that that portion of the glycerides dissolved by ethyl or methyl alcohol is richer in volatile acids than the undissolved portions. The iodine number of the dissolved fat is less than the undissolved fat. The melting-point of the fats dissolved by alcohol is less than that of the undissolved fats.

The above facts would be of importance in the examination of butters, to which it is suspected artificial butyrates may have been added.—(Abstract from the *Analyst*, vol. xiii., p. 55).

A Quick Method of Distinguishing Oleomargarine in Butter.

Dubernard has proposed the following method for a qualitative examination of butter for oleomargarine. The method rests upon the observation that pure butter vigorously shaken with ammonia at a temperature of from 70° to 80° and afterwards heated to 100° produces only a small amount of foam, which does not last a long time. Margarine, on the contrary, produces a large quantity of lasting foam. In order to distinguish butter from margarine by this method, the following manipulation is pursued.

In a test-tube place about 3 grms. of the butter to be examined. Heat to 95° or 100° in a water-bath, and then allow to cool to about 80°. Add to the melted substance 5 c.c. of ammonia, shake vigorously, and place again in the water-bath and heat to 95° or 100°. The ammonia is volatilised with the formation of foam. The foam in the tube rises more or less according as the butter contains a larger or smaller quantity of oleomargarine. In mixtures of pure butter with known quantities of margarine the tube can be graduated and the relative quantities of butter and margarine thus approximately determined.—(Abstract from *Chemiker Zeitung*, 1888, No. 46, p. 760).

Detection of Adulterations in Butter.

Bockairy proposes the following method for the detection of adulterations in butter which rest upon the different solubilities of fats in toluene:—

Place in a test-tube 15 c.c. of pure toluene, add 15 c.c. of the filtered fat and 40 c.c. of strong alcohol at 18°; the toluene holding in solution the fatty matter remains at the bottom of the tube. By means of a water-bath the tube is heated to 50° and thoroughly shaken. If the sample is of butter fat or a mixture of butter fat and some other kind, there is no turbidity; but if no butter be present a turbidity is at once manifested. The tube is placed in water at a temperature of 40° for half an hour; pure butter gives no turbidity at the end of that time, but if other fats are present the mixture will appear turbid.—(Abstract taken from the Chemical News, July 6, 1888, p. 11, and *Bul. de la Société Chimique de Paris*, vol. xlix., No. 5, p. 331).

Difference Between Natural and Artificial Butter.

C. J. van Lookeren proposes the following for a characteristic test between pure and falsified butter:—

A small amount of butter is melted in a teaspoon, and a drop thereof placed in boiling water contained in a watch-glass. If the butter be pure a thin film of fat is formed upon the hot water, which breaks up into numerous fat globules, which tend to collect quickly at the periphery. With oleomargarine, &c., a thin film of fat is formed in the same way, which, however, breaks up into only a few large drops, which remain distributed over the whole surface of the water. The conditions for the success of the experiment are that the water be perfectly pure and clear, and the melted butter fat very hot.—(Abstract in the Repertorium of the *Chemiker Zeitung*, No. 18, 1888, p. 143, from the *Milchstg.*, 1888, No. 17, p. 562).

A Modification of Koettstoefer's and Reichert's Processes.

Lowe has proposed the following method of determining

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

the volatility and saponification equivalent of butter and other fats :—

About 2 grms. of the filtered fat are saponified with 10 c.c. of normal alcoholic potash in a stoppered flask. The alcohol is then boiled off and the soap dissolved in 50 c.c. of hot water. The excess of potash is then determined with semi-normal sulphuric acid solution. The saponification numbers having thus been determined, enough additional sulphuric acid is run in to make 25 c.c. in all. The flask is then connected to a condenser, and 50 c.c. distilled off, filtered, and determined in the usual way. The same flask is used throughout the whole process, one of 200 c.c. capacity answering the purpose very well. The whole process does not occupy more than two hours, and can be completed often in less time.

Tyrer, criticising the process of Mr. Lowe, was of the opinion that the quantity of fat taken, two grms., was too small, since it gave only about one-tenth of a grm. of volatile fatty acids. The alkali also dissolved some of the glass, thus introducing an error of which no account was taken. Carbonic acid, moreover, expelled by this method, increased the apparent estimate of filtered fatty acids.—(Abstract from the *Journal of the Society of Chemical Industry*, March, 1888, p. 185; May, 1888, p. 376).

Saponification Without the Use of Alcohol.

Mansfeld, in order to avoid the losses due to etherification during saponification in the presence of alcohol, has proposed to carry on the process of saponification, preparatory to the estimation of volatile acids in butter, without the us of alcohol. The method employed is as follows :—

Five grms. of the melted and filtered butter fat are taken; into the melted fat are allowed to run 2 c.c. of a potash lye containing 100 grms. caustic potash in 100 c.c. of water. The flask is closed with a stopper carrying a glass tube drawn out to a capillary point; the flask is then placed in an air-bath heated to about 100° and allowed to remain for two hours. At the end of that time the saponification is completed. One hundred c.c. of water are now added, the flask placed in a water-bath until the soap is dissolved, which is decomposed and subjected to distillation in the usual way.—(Abstract in *Chemisches Central-Blatt*, June 23, 1888, p. 870, from *M. Z.*, No. 17, pp. 281—83).

Wollny's Criticism of the Reichert-Meissl Method.

The method of determining volatile fatty acids devised by Reichert has, during the past year, been subjected to an extended criticism by Dr. R. Wollny, of Kiel. Dr. Wollny, as a result of 98 analytical tests, was convinced of the truth of the statement of Professor Fresenius, that the Reichert method was totally unreliable for the determination of very small quantities of butter in oleomargarine.

As a result of his analytical work Dr. Wollny was convinced that the chief source of error in the Reichert work was due to the absorption of carbonic acid. He asserts that the error which may arise from this source must amount to as much as 10 per cent butter, and renders the results obtained by the method quite inaccurate. It being very difficult to secure an alkali free from carbonate, the author decided to use a 50 per cent solution of caustic soda instead of potash, since in a solution of that strength the chloride, nitrate, sulphate, and carbonate of soda are quite insoluble.

An arrangement was also devised by which the solution of caustic soda could be kept and drawn off for use without risk of absorption of carbonic acid. Such a solution made and kept in this way gave for 3 c.c. treated by the ordinary process of Reichert's distillation, an amount of volatile acid sufficient to neutralise from 0·2 to 0·3 c.c. of the decinormal barium hydrate solution. The author's precautions to prevent absorption of CO_2 are wholly unnecessary when the saponification is carried on in closed flasks.

Dr. Wollny further discusses the errors due to the formation of butyric ethers during saponification and distillation, and also the error due to the mechanical translation of particles of insoluble fatty acids during the process of distillation, and the error due to the shape and size of the vessel in which the distillation is carried on and the time of its duration. The magnitude of these errors he states as follows :—

(1). Due to absorption of carbonic acid + 10 per cent (2 and 3). Formation of butyric ether − 13 per cent. (4). Cohesion of fatty acids − 30 per cent. (5). Shape and size of vessel + or − 5 per cent.—(*M. Z.*, 1887, Nos. 32, 33, 34, 35, and the *Analyst*, 1887, Nos. 139, 140, 141, 142).

Dr. Wollny further describes the exact methods to be employed in the examination and the results obtained, for the details of which I refer to the original papers.

As president of the butter commission of the German Dairy Association, Dr. Wollny has proposed the following method to be employed in the comparative examinations of butter for the forthcoming report of the commission (see *M. Z.*, No. 25, 1888). In the preparation of the decinormal barium solution each one of those taking part in the analyses has been furnished with samples of normal sulphuric acid, pure crystallised chloride of barium, and pure peroxalate of potash. In addition to this for testing the refractometer samples of olive oil, nitrobenzol and monobromnaphthalin have been sent. Following are the details given by Dr. Wollny for the preparation of the reagents and the conduct of the analysis.

METHOD PROPOSED BY DR. WOLLNY FOR THE EXAMINATION OF BUTTER FOR THE COMMISSION OF THE GERMAN DAIRY UNION.

(From the *Milch Zeitung*, 1888, No 25 et seq.).

1. *Proving the Weights and Burettes.*

The weights which are to be used must be carefully compared and the burettes calibrated.

2. *Estimation of the Strength of Normal Sulphuric Acid.*

A clean dry dropping-bottle of about 60 grms. content, the tip of which is touched with vaseline on the outside, is carefully weighed; 35 or 40 grms. of normal sulphuric acid are then placed in it, and it is again weighed. Afterwards five portions in duplicate of about 3 grms. are weighed in a beaker glass of 300 c.c. capacity. The drop-bottle being weighed after each portion, the exact weight of the normal sulphuric acid is determined. One hundred c.c. of recently boiled distilled water are added to each of the portions. One hundred c.c. of this distilled water must not require more than 2 drops of barium solution to give colour after 1 c.c. of the phenolphthalein solution has been added. The samples are heated in the water-bath to the boiling-point, and to each portion as many c.c. of dilute barium chloride solution added that for each grm. of the normal sulphuric acid there are present 10 c.c. of the $BaCl_2$. The barium chloride solution contains 15 grms. of the salt in 1 litre of distilled water. Afterwards the beakers are covered with watch-glasses and allowed to stand for fifteen minutes over the water-bath. The precipitates are to be collected upon ash free filters of 9 centimetres diameter, and washed with hot distilled water until the chlorine action disappears. After drying and incineration the weight obtained is to be multiplied by the factor 0·34331. The five duplicate portions, after the addition of one c.c. of phenolphthalein solution, are treated with barium solution until the red colour appears. The numbers obtained are to be calculated to 100 grms. of the normal sulphuric acid.

3. *Estimation of Saturation of the Normal Sulphuric Acid by the Barium Solution.*

From the results obtained by the above analyses the exact strength of the decinormal barium solution is to be determined.

4. *Titration of Barium Solution with Potassium Peroxalate.*

One grm. of the peroxalate of potassium, after drying for twelve hours in a desiccator over sulphuric acid, is placed in a weighing bottle similar to the one described above. Sixty grms. of hot distilled water are then added, and after the salt has been dissolved and the solution cooled the weighing-bottle is again weighed. About 12 grms. of the solution are now run into each of five beaker glasses, and the exact amount in each one determined by re-weighing the weighing-bottle. Ninety c.c. of recently boiled distilled water are now added, together with one c.c. of phenolphthalein solution. The barium solution is now added until the red colour, which at first disappears, remains for at least five minutes. The results are calculated to the strength of the barium solution according to the formula—

$$T = \frac{10000 \times p\ (b-t)}{84{\cdot}5\ n\ (l-t)},$$

in which

t = the weight of the weighing-bottle empty.
b = the weight of the weighing bottle + the peroxalate.
l = the weight of the weighing bottle + the peroxalate solution.
p = the weight of the portion of the solution employed.
n = the number of c.c. of barium solution used.

5. *Estimation of the Volatile Acids after Saponification with the Aid of Alcohol.*

Five grms. of the butter fat are weighed into an Erlenmeyer flask; 10 c.c. of alcohol at 96 per cent, and 2 c.c. of concentrated soda lye at 50 per cent, which has been preserved in an atmosphere free of carbonic acid, are added. The flask, furnished with a reflux condenser, is heated, with occasional shaking, in a boiling water-bath for one-quarter of an hour. The alcohol is then distilled off by allowing the flask to remain for three-quarters of an hour in a boiling water-bath. One hundred c.c. of recently boiled distilled water are then added and allowed to remain in the water-bath until the soap is dissolved. The soap solution is then immediately decomposed with 40 c.c. of dilute sulphuric acid (25 c.c. sulphuric acid to 1 litre), and the flask immediately connected with the condenser. This connection is made by means of a 7 m.m. diameter glass tube, which, 1 c.m. above the cork, is blown into a bulb 2 c.m. in diameter; the glass tube is now carried obliquely upwards about 6 c.m. and then bent obliquely downward; it is connected with the condenser by a not too short rubber tube. The flask is now warmed by a small flame until the insoluble acids are melted to a clear transparent liquid. The flame is now turned on with such strength that within half an hour exactly 110 c.c. are distilled off. 100 c.c. of the distillate are now filtered off, placed in a beaker glass, 1 c.c. of phenolphthalein solution added, and titrated with barium solution; when the red colour is shown the contents of the beaker glass are poured back into the measuring glass in which the 100 c.c. was measured, again poured back into the beaker, and again titrated with the barium solution until the red colour becomes permanent. The distillation should take place in as nearly thirty minutes as possible.

6. *Estimation of the Volatile Acids after Saponification without Alcohol.*

Five grms. of the butter fat are saponified with 2 c.c. of concentrated potash lye preserved from contact with carbonic acid. The lye solution is made by dissolving 100 grms. of the potash in 58 grms. of water. By gentle rotation of the flask the lye and fat are intimately mixed together; the flask is then placed in a vertical position over a boiling water-bath until the mixture becomes solid. It is then placed obliquely in the water bath. After it has remained here for two hours it is taken out and the remainder of the process continued as above.

7. *Estimation of the Mean Molecular Weight of the Volatile Fat Acids.*

The soap solution obtained by the titration of barium hydrate in No. 6 is placed in a weighed platinum dish, evaporated to dryness in the water-bath, dried in a drying oven for two hours, and again weighed.

8. *Estimation of Volatile Fat Acids by Distillation from Magnesium Salts.*

Eight grms. of butter fat are placed in an Erlenmeyer flask, treated with 3 c.c. of concentrated potash lye and 15 c.c. of alcohol, as in No. 5, and the alcohol then distilled off. The soap, dissolved in 100 c.c. of water, is washed with 250 c.c. of water in a measuring flask of 500 c.c. capacity, and cooled to the temperature of the room. Then, by means of a pipette, with constant shaking, 50 c.c. of magnesium sulphate solution, 15 per cent strength, are added, the flask filled up to the mark with water, and vigorously shaken. The mixture is now placed upon an 18 centimetre filter and 300 c.c. filtered into a measuring flask. The filtrate is brought into a flask holding about 500 c.c., which on the one side is joined with a steam generator and on the other with a condenser. 2 c.c. of strong sulphuric acid, together with two pieces of pumice stone, are added. 250 to 275 c.c. are now distilled off into a measuring flask of 500 c.c. capacity, the distillate being filtered into the flask through a moistened filter. The gas flame under the distillation flask is then turned down low and the distillation continued in a current of steam until the 500 c.c. flask is full. After the filter which has been used has been washed with a little water, the distillate is placed in a large flask of 1 litre capacity and 2 c.c. of phenolphthalein added and titrated.

9. *Estimation of the Volatile Fatty Acids from Copper Salts.*

The estimation is carried on exactly as in No. 8, substituting 50 c.c. of copper sulphate solution for the 50 c.c. of magnesium salts. In the present case the distillate may be collected directly in the one half-litre flask without filtration, since by precipitation with copper sulphate solution no insoluble fatty acids pass over during distillation.

10. *Estimation of Volatile Fatty Acids by Distillation in a Current of Steam, according to Goldmann.*

Five grms. of butter fat are weighed in a long-necked flask of about 300 c.c. capacity. 10 c.c. alcohol and 2 c.c. potash lye are added, and the flask connected, on the one hand, with a steam generator, and on the other with a condenser. The contents of the flask are now warmed with a small flame for twenty minutes, the condenser being directed obliquely downward, and, in a measuring cylinder, 6 c.c. distilled off. The steam is then directed into the flask and 50 c.c. more collected. The soap is now decomposed with 5 c.c. of sulphuric acid (20 c.c. strong acid diluted to 100 c.c.), the separated fat acids heated with a small flame until they form a clear solution, and in a current of steam the volatile acids distilled off into a 500 c.c. flask. The size of the flame is so regulated that the contents of the distillation flask remain constant at about 30 to 40 c.c., and the distillation is continued until each succeeding 500 c.c., after the addition of 2 c.c. phenolphthalein solution, require not more than 2 c.c. of the decinormal barium solution to produce the red colour.

12. *Estimation of the Fatty Acids Soluble in Ten Per Cent Alcohol.*

(*a*). *Rose's Method.*—12·5 grms. of butter fat are weighed into a graduated flask of 500 c.c. capacity, 50 c.c. of alcoholic potash lye (about 112 grms. of potassium hydrate dissolved in absolute alcohol and made up to 1 litre) are added and gently shaken. After five minutes as slight an excess of semi-normal sulphuric acid as possible is added. After two minutes dilute with water to 490 c.c.;

to destroy the foam, add 5 c.c. more absolute alcohol, fill up to the mark with water, aad then add as much more water as will correspond to the amount of fat taken. The flask is now shaken, contents filtered through a dry filter, and 250 c.c. of the filtrate titrated with decinormal potash lye.

(*b*). *Modification of the Above Process by Dr. Wollny.*—Weigh 6·25 grms. of the fat in an Erlenmeyer flask of 300 c.c. capacity. Add 25 c.c. of potash lye, made with absolute alcohol as described above, and then diluted with absolute alcohol until not more than 74 c.c. and not less than 73 c.c. of semi-normal sulphuric acid are required to neutralise it. The flask is then closed with a stopper which carries a glass tube 10 m.m. wide and 50 c.m. long; heat with a very small flame until the contents are near the boiling-point for about twenty minutes, and until the smell of the butter ether has entirely disappeared. The flask is then cooled in water and 150 c.c. of recently-boiled distilled water added. When the soap is dissolved and the whole mass cooled to about 15°, 75 c.c. semi-normal sulphuric acid are added. The flask is then closed with a rubber stopper and shaken vigorously for one minute. Filter through a strong dry-folded filter into a graduated flask holding 200 c.c., pour the 200 c.c. into a large beaker glass, and titrate with barium solution.

13. *Estimation of Insoluble Fat Acids.*

Treat 3 to 4 grms. of the butter fat with 2 c.c. concentrated soda lye and 10 c.c. alcohol in a porcelain dish on the water-bath and evaporate the soap to dryness. Dissolve the soap with 100 c.c. of hot water and 5 c.c. concentrated sulphuric acid, and heat the separated fatty acids for one hour on the water-bath. Pour the contents of the dish on a filter of 11 c.c. diameter, made of the best thick Swedish filter-paper, previously dried and weighed. Upon this filter the acids are washed with 1·5 litres of boiling water. The filter with the insoluble fatty acids, after they have been solidified, is placed in a weighed beaker glass, dried for two hours in an air-bath, and weighed.

16. *Estimation of the Free Fat Acids.*

Ten grms. of the butter fat are placed in a beaker glass with 20 c.c. of ether and 10 c.c. of alcohol and 1 c.c. phenolphthalein solution. The free acids are then titrated with decinormal alcoholic potash.

11, 14, 15, 17, 18, 19. *Combined Estimation of the Saponification Number, the Volatile, Soluble, and Insoluble Fat Acids.*

(*a*). *Saponification Number.*—Five grms. of the fat are weighed into an Erlenmeyer flask and 25 c.c. of alcoholic potash added. (25 c.c. alcoholic potash should saturate from 48 to 50 c.c. semi-normal sulphuric acid). The mixture should be warmed as in No. 5 for a full hour with the reflux condenser. Meanwhile, the same quantity of alcoholic potash should be exactly titrated with the semi-normal sulphuric acid, and later being titrated by the barium solution used and the number obtained noted. The alcoholic soap solution is taken from the water-bath, the solid parts adhering to the walls of the flask dissolved by gentle shaking, and, after the addition of 1 c.c. phenolphthalein solution, titrated with semi-normal sulphuric acid. The number obtained is subtracted from the number obtained in the blank experiment and calculated back to the corresponding number of c.c. barium solution.

(*b*). *Volatile Fat Acids.*—The alcohol is driven off from the exactly neutralised alcoholic soap solution obtained in the foregoing experiment, and then an additional amount of sulphuric acid added, amounting to 2 c.c. more than necessary to neutralise the original potash lye employed. The mixture is then diluted with 140 c.c. of recently-boiled distilled water and two pieces of pumice stone added, and, as in No. 5, 110 c.c. distilled off, of which 100 c.c., after filtration, is titrated.

(*c*). *Soluble Fat Acids.*—After the end of the foregoing experiment the distillation flask is removed from the distillation tube and replaced by one filled with distilled water, and placed as a receptacle under the condenser. The condensation water is now allowed to flow from the condenser, and the condensed insoluble fatty acids driven over into the original distillation flask by a current of steam. In like manner the insoluble acids collected upon the filter are washed into the original distillation flask. After the fatty acids are solidified the whole of them are brought into a cylinder 3·5 c.m. wide and 15 c.m. long, which ends in a 6 m.m. wide tube carrying a goose-necked glass tube from its side; and on the lower end is closed with a rubber tube and pinch-cock. The lower contraction of the cylinder is stopped with a plug of glass wool, which forms a thick filter but allows hot water to run through easily. Under the goose neck of this wash vessel, which is held in a vertical position by a retort holder, is placed a graduated flask of 500 c.c. capacity, into which the excess of water flows. When the acids have been brought from the distillation flask, together with the pieces of pumice stone, into the wash-flask, any residue is washed out with the washing-bottle with boiling water. The above must be so conducted that no drops of the fatty acid pass through the glass wool, and that no fatty acid remains on the upper walls of the washing-flask. The washing-flask is furnished with a gum stopper carrying two holes. Through the one passes a tube for the inlet of steam: through the other a tube at least 8 m.m. in diameter, cut off obliquely at the lower end and divided above the stopper into two branches. By means of one of these branches it is connected with a perpendicular condenser, at least 8 m.m. wide, and through the other it is connected by means of a rubber tube and pinch-cock with a hot-water reservoir by means of a U-tube reaching to the bottom thereof. Through the steam-tube, which is somewhat bent at the end, so that the steam is directed obliquely downwards and outwards against the sides of the washing-bottle, a current of steam is conducted, which stirs up in a lively manner the surface of the fatty acids, which swim upon the top of the water, while the condensed water drops back out of the reflux condenser in a boiling hot condition, and the excess flows through the goose-neck into the measuring flask. The wash-water collected in the 500 c.c. flask is titrated with barium solution, with the addition of 2 c.c. phenolphthalein solution. This operation is repeated three times, in all, 1·5 litres of wash-water being collected. The total amount of barium solution required in the three operations is collected in one number.

(*d*). *Insoluble Fatty Acids.*—After the end of the foregoing experiment the wash-flask is cooled until the fatty acids are solidified. The pinch-cock closing the lower opening of the wash-flask is opened, the water allowed to flow off, and a current of air passed through the apparatus by means of an aspirator after the opening of the goose-neck is lightly stoppered and the steam generator removed. The wash-flask, together with the fatty acids and the glass-wool plug, are completely dried in this manner after, at most, half an hour. The steam generator is now replaced with a flask which contains ether free of water, alcohol, and acids. The ether is brought to the boiling-point by means of warm water, and its vapour, condensing in the washing-flask, dissolves the fatty acids and carries them into the weighed flask of about 100 c.c. capacity, placed below to receive them. When about 40 or 50 c.c. of ether have distilled over, the operation is broken, the outer end of the wash-flask washed with ether, and the weighed flask below is placed in a warm place in order to drive off the ether. The weighed flask containing the acids is now warmed in the water-bath and placed under the receiver of an air-pump. After the acids are completely freed from ether by this method the flask is again weighed and the weight of the acids noted

(*e*). *Mean Molecular Weight of the Insoluble Fat Acids.*—The fatty acids obtained in the foregoing experiment are melted at a low temperature and from 0·8 to 1 grm

weighed in a beaker glass, dissolved in 50 c.c. of alcohol, 1 c.c. phenolphthalein solution added, and titrated with barium solution.

20. *Determination of the Iodine Number.*

Weigh out from 0·8 to 1 grm. butter fat in a flask of about 200 c.c. capacity, furnished with a glass stopper; dissolve in 10 c.c. chloroform and add 20 c.c. iodine solution. In case the liquid is not clear, more chloroform must be added. If the iodine colour should rapidly disappear, add from 5 to 10 c.c. more. The amount of iodine added should be sufficient to secure strong colourisation after standing two hours. Add 10 to 15 c.c. iodide of potassium mixture and 150 c.c. of water; titrate with thiosulphate of sodium solution until the iodine has almost disappeared. Add then a little starch solution, and continue titration until the blue colour has disappeared.

21. *Estimation of Refractive Index.*

Set the large Abbe refractometer with water at 18°, so that the index reads 1·3330. The instrument should then be placed in a room which is kept at a temperature of about 25°. The estimation of the refractive index of butter fats cannot be made below 25° on account of the solidification of the fat. The instrument is also to be tested at 20° with olive oil, nitrobenzol, and monobromnaphthalin.

25. *Determination of the Specific Gravity at Zero or 15°.*

A platinum crucible is supplied with a platinum wire handle, so that it can be suspended from the hook of the balance. It is then weighed empty, and afterwards its specific gravity taken in water at zero. The water is kept at zero by being placed in a small beaker glass, which in turn is put in a larger beaker, closed and surrounded with finely pounded ice. The crucible is then dried and 15 grms. of melted butter fat placed therein. The butter fat is allowed to solidify slowly at a temperature not below 15°. The crucible with its contents is then weighed in the air and placed in distilled ice-cold water for an hour. The whole is then weighed in water at zero as before. From these results the specific gravity of the fat at zero is determined. In the same way determine the specific gravity at 15°.

26. *Estimation of the Specific Gravity in Boiling Water by means of the Pyknometer.*

A small flask of 50 grms., the neck of which is drawn out to a narrow tube and marked at the narrow place, is weighed empty. It is then filled with distilled water to the mark and placed for an hour in finely pounded ice. The contraction of the water is restored by the addition of ice-cold water until the mark is reached; it is then dried, allowed to come to the temperature of the room, and weighed. The same flask is then filled to the mark with boiling water, and, after coming to the temperature of the room, weighed. The flask is then emptied, dried, filled with melted butter fat, kept in a boiling water-bath for an hour, the butter fat filling to the mark, afterwards cooled to the temperature of the room and weighed.

27. *Estimation of the Specific Gravity with Mohr's Balance.*

This is determined in the usual manner by the use of a specific gravity bob, the thermometer of which is arranged so as to show a temperature of 100°.

28. *Estimation of the Specific Gravity with the Areometer in Boiling Water.*

This is determined by means of spindles furnished by the firm of G. C. Gerhard, in Bonn. These spindles are graduated especially for specific gravity at a temperature of 100°.

29. *Estimation of the Melting-point.*

This is determined in straight or U-formed capillary tubes. They are filled with butter fat at 100° and placed in ice-water for a quarter of an hour. The capillary tube is then placed, with a thermometer, in a beaker glass with water at 20° and slowly warmed with a small flame.

30. *Estimation of the Solidifying Point.*

Place about 100 c.c. of the melted fat in a test-tube at 40°. Stir with a thermometer until the fat begins to solidify, the test-tube meanwhile being placed in a large vessel containing water at 20°. The temperature will rise slightly when the solidification begins, and the highest point reached is entered as the solidification point.

Note. Dr. Wollny has proposed in the above scheme an exhaustive study of butter fat. Many points appear to be superfluous and others elaborated into unnecessary detail. The method of determining insoluble fatty acids appears to be more objectionable than any other part of the scheme. The method of making the melting-point first described in the *Journal of Analytical Chemistry* (vol. i., No. 1, p. 39) appears to have escaped the notice of the German commission. I also note with regret the apparent ignorance of the existence of the Gooch crucible existing in Germany.

Points to be especially commended in these investigations are, sending samples and standard reagents, blanks for entering the analytical results, and minute printed directions for conducting the manipulation.

The numbers prefixed to the several paragraphs correspond to the number of the column in the blank in which the results are to be entered.—H. W. W.

(To be continued).

THE PROPOSED CHEMICAL LABORATORY AT THE UNIVERSITY OF SYDNEY.

We are indebted to the courtesy of Professor A. Liversidge, F.R.S., for a very full description of the projected laboratory. The matter, he tells us, was in contemplation as far back as 1873, but unfortunately certain makeshifts were found possible, and so the erection of a really suitable building has been proposed. Happily, says Professor Liversidge, such expedients are now no longer possible.

Funds do not allow of the erection of a palatial structure, and the University is right in not sacrificing practical utility to outside display.

The main laboratory, intended for all save the very junior students and for a select few who are sufficiently advanced to undertake original research, is 72 by 36 feet, and 22 feet high in the centre. Part of the roof will be left flat for experiments requiring direct sun-light. There will be no provision required for warming the rooms, as on the few days when artificial heat is desirable movable gas stoves will be placed in the lower part of the draught-cupboards.

At one end is a yard for out-door experiments, with a large sink, a good water-supply, and generators and a gas-holder for sulphuretted hydrogen. The floors will be of wood, varnished round the walls and the benches. All the interior wood work will also be varnished. On the roof or in a tower will be a large cistern to supply water under pressure. The gas and water-pipes, battery, telephone and electric light wires, are to be laid in channels along the floors and down the angles of the walls. A well, passing down from the tower to the basement, will serve for aspirator and compressed air tubes. Some of the windows are utilised as draught-cupboards by enclosing the outer side of the lower sash. Others can be used for microscopic work. There is at one end of a long slate bench a

sink (Doulton ware) with the edges protected by wood and india-rubber, with a drying slope and rack. Next follows a self-feeding still for distilled water supplying ten gallons a day.

The principal lecture room is 34 by 47 feet, and is arranged for 180 students. The lecture table, 27 by 3 feet, is provided with gas and water, leads for the electric light, aspirators, air-blasts, oxygen, hydrogen, and coal-gas under water pressure from the cistern. There will be a lecture-preparation room, a collection-room and museum, a smaller lecture or class-room for 130 students, a demonstration room for juniors, 36 by 24 feet, and separate balance rooms, rooms for reference library, for gas analysis, spectroscopic and polariscope work, and a dark room.

The metallurgical and mineralogical laboratories are in the basement, fitted with a gas-engine and crushing and grinding apparatus, two 9-inch and two 12-inch furnaces, and two muffle furnaces on Percy's design. On the ground floor at the south end are the Professor's private room, 21 by 16 feet; a microscope and balance room of the same dimensions, and a private laboratory, 32 by 21 feet, where three or four advanced students can work under the immediate eye of the Professor.

From the very full description and the twelve accompanying plates we must conclude that the laboratory, if carried out as proposed, will be a credit to the University, and will give good scope both for instruction and for research. The space available seems to be well utilised, and there are all necessary appliances, without anything which the economist can denounce as luxurious or extravagant.

The new laboratory will be very near the biological, the physical, and the engineering laboratories, an arrangement which may often prove a mutual convenience.

NOTICES OF BOOKS.

The British Journal Photographic Almanack, and Photographer's Daily Companion, 1889. Edited by J. Traill Taylor. London: Greenwood and Co.

If anyone doubts the importance which photography has reached, a glance at this almanack, and especially at its advertising pages, will convince him of his mistake. If we leave out of consideration lenses, lamps, dry plates, sensitised papers, chemicals, and complete sets of apparatus, we find here no fewer than ninety cameras, each recommended as possessing some advantageous feature, or as being adapted for some special purpose. It has, in fact, been found so difficult to find out rational, appropriate names for these devices, that one inventor gives to his instrument the ill-omened name of "international."

In the almanack itself we find some very interesting matter. A sceptically disposed individual doubts if "detective" cameras have ever really detected or helped to detect a single evil-doer?

A little poem by Mark Oute, entitled "My Detective," reminds us that even in England the doings of the photographer may be annoyingly interfered with by Jacks-in-office.

A short paper on "Chemical Changes," by Mr. C. H. Bothamley, F.C.S., has a wide bearing; it may concern all, or most of the chemical arts. It brings forward facts which, though well known to professional chemists, are often overlooked by outsiders.

Mr. J. Hubert writes anent the intrusion of amateurs, one of whom had kindly offered to photograph a religious gathering at cost-price, *plus* a champagne supper!

In proof of the greater activity of the light in India, we find it mentioned that one twenty-fifth of a second was an amply sufficient exposure for obtaining a good seascape at Madras.

To all persons interested in photography this almanack will prove invaluable, but we trust that they will not be bewildered with choice among the multitudinous appliances here recommended.

Our Supply of Phosphates for the Manufacture of Superphosphate and other Manures. By Hermann Voss. London: Farquharson, Roberts, and Phillips, Limited.

This pamphlet comprises a paper read on December 10th last, before the Chemical Manufacturers' Association and the discussion which followed.

The author shows that the supply of mineral phosphates is by no means unlimited. Our imports from Canada do not exceed 20,000 tons yearly. The shipments of Norwegian apatite and Russian coprolites have almost ceased. The Estremadura phosphates are in great part of low quality, and the expense of transport is great. The largest importations have been of late from Carolina, whence, in 1887, we drew no less than 164,000 tons. Nor is an early exhaustion of the deposits probable. But, on the other hand, the demand for this material in America is fast increasing, and the freight is generally high.

The Belgian phosphate is described as abundant in quantity but very rich in calcium carbonate, a so-called "profligate" ingredient, since it involves the waste of a large amount of sulphuric acid. The total quantity of phosphates imported into the United Kingdom in 1887 was 283,415 tons.

We are glad to find that the author, in passing, enters his protest against the waste of fertilising matters, phosphates among others, going on in this country. The facts stated in the paper and in the discussion may, perhaps, convince some persons concerned, that this extravagance cannot go on for ever. Other countries are now rivalling us in the folly of pouring fertilising matter into the sea, heedless that the time must come when the Bank of Nature will no longer honour our drafts.

A New Patent Calendar for 1889. Thos. Fletcher and Co., Warrington.

Almanacks have already come into very general use as channels for advertisements. That of Messrs. Fletcher, now before us, present a novel feature. There is a page for every working day in the year, and on each we find a figure of one of Messrs. Fletcher and Co.'s devices for the production of heat by means of gas—scientific, technical, culinary, or generally domestic. For descriptions the reader is referred to the "Complete List" issued by the firm. At the foot of the page follow the day of the month and the week.

Letts's Diaries for 1889.

We have received a few of these useful publications from Messrs. Cassell, Petter, and Galpin, and perceive that they keep up to their usual style of excellence.

CORRESPONDENCE.

ELECTRIC SUGAR.

To the Editor of the Chemical News.

Sir,—The *Times* of Saturday, January 5th, contains an account from Philadelphia of the collapse of the "New York Electric Sugar Refining Company," in which the writer says—"Quantities of refined sugar, chiefly cubes, had been purchased by the operators and prepared in some secret spot with a chemical liquid which eliminated the ordinary impurities found in all sugars" . . . "the chemical used had crystallised the cubes to a large extent,

and they had a finer appearance and a finer quality than sugar was ever known to possess."

From this latter statement it would appear that the chemical process contained some elements of value and apparently unique as to the results. Can any of your readers throw light on this particular process? or has the secret perished with the decease of the inventor?—I am, &c.,

G. A. Keyworth.

Hastings, January 7, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cvii., No. 26, December 24, 1888.

This issue contains merely an account of the Annual Public Session of the Academy on December 24, with a report of the "allocution" of the President, and notices of the prizes awarded.

Moniteur Scientifique, Quesneville. Series 4, Vol. ii., November, 1888.

The Yeasts of Wines.—Louis Marx.—The author recapitulates the results of Hansen, who found in beer-yeast, previously regarded as pure, six ferments, *Saccharomyces pastorianus* I. II. III., *Saccharomyces cerivisiæ*, *Saccharomyces ellipsoideus* I. and II., distinguished by the time which they require for the development of their ascopores. In the lyes of certain wines he distinguishes no fewer than fifteen ferments, to which he does not assign names, as he has not yet decided whether the forms obtained from different wines are identical.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—This paper does not admit of useful abstraction.

Synthetic Formation of Closed Carbon Chains in the Aromatic Series.—W. H. Perkin.—From the *Journal of the Chemical Society*.

Improvements in the Manufacture and Use of Explosives.—Oscar Guttmann.—The author describes an improved method for making charcoal, patented by Güttler, of Reichenstein. He introduces hot carbon dioxide into the retorts during the process of charring, and cold carbon dioxide during cooling. The product from lime-kilns is sufficiently pure. He next notices the discrepancies observed in the analysis of gun-cotton, and points out the necessity of using absolutely pure reagents. He then describes the carbo-dynamite of Borland and Reid, which, it is said, can be exploded in a coal-mine without exploding fire-damp; a new explosive made by Schückher and Co., under the name of meganite; the "bellite" of Carl Lamm, of Rotebra; the "Security" of Schœneweg; the "Romite" of Sjöbrg (?); the "Roburite" of C. Roth; the explosives of R. K. Punsheon, of Sir F. A. Abel, and of Grüne, &c.

Industrial Review and Various Patents.—Abstracts of a number of German specifications, largely referring to colouring-matters.

Industrial Society of Mulhouse.—Session of September 12, 1888.—The principal feature of the session was a paper by P. Richard on the chemical constitution of wool, which he regards as an amidic acid.

Action of Sulphur upon the Oils.—C. A. Fawsitt, F.R.S.E., F.C.S.—From the *Journal of the Society of Chemical Industry*.

Thiophosphoryle Fluoride.—Prof. T. E. Thorpe, F.R.S., and J. W. Rodger.—From the *Journal of the Chemical Society*.

Resistance of Dressing to the Bleaching Processes, and on the System of H. Kœchlin and Mather and Platt.—Camille Kœchlin.—The essential feature of this process is the use of caustic soda at 25 grms. a litre, when a previous treatment with lime is unnecessary. He shows that sulphuric acid has a less injurious effect upon textile fibres than it is commonly supposed, and is more easily removed by washing than are the volatile acids.

Proportion of Ash in Human Bones at Different Ages.—W. P. Mason.—From the Chemical News.

New Method for the Purification of Alcohol or the Production of Non-poisonous Alcohol.—Emile Reboux.—The author passes in review the methods of Godefroy (use of a mixture of zinc-powder with copper and a hypochlorite), that of Bowick, Bang, Ruffin, and Philippart. P. F. Tettelin, instead of transforming or eliminating existing impurities at the risk of destroying at the same time the peculiar aroma of each spirit, professes to prevent the formation of furfurols, aldehyds, superior alcohols, and alkaloids.

Test for Essential Oils.—"Eck" founds a process for detecting the oil of pine when used for sophisticating the oil of juniper berries upon the power of the latter of at once decolourising a very dilute alcoholic solution of juniper, whilst many essential oils do not show this reaction. The method of applying the test is to dissolve a drop of the oil in question in 3 c.c. of alcohol at not less than 90 per cent, and to add a drop of the tincture of iodine. In a check experiment, in which he added directly oil of turpentine to oil of juniper and applied the iodine test as above described, the iodine was nevertheless decolourised. In consequence he distils the oil on the water-bath and applies the test to the first drop which comes over. Iodine is instantly decolourised by oil of peppermint (Mitcham); in a minute by the oils of ginger and juniper; in two minutes by oils of pepper and cardamum; in three to eight minutes by oil of mace. The oils of coriander, carraway, turpentine, rue, sassafras, roses, rosemary, orange, aniseed, fennel, angelica, and wormwood do not decolourise iodine.

Archives Neerlandaises des Sciences Exactes et Naturelles. Vol. xxiii., Part iii.

This number contains no chemical matter.

MISCELLANEOUS.

Society of Arts.—The following arrangements have been made for the Wednesday Evening Meetings of the Society of Arts after Christmas. On the 16th January, a paper will be read by Colonel Hozier, on the "Channel Tunnel;" on the 23rd one by Professor George Forbes, on "Electric Meters for Central Stations;" and on the 30th one by Mr. Conrad Beck, on the "Construction of Photographic Lenses." Papers for which dates have not yet been fixed will also be read on the "Status of the County Council," by Mr. G. L. Gomme; on the "Forth Bridge," by Mr. B. Baker; on "Salt," by Mr. P. L. Simmonds; on the "Manufacture of Aluminium," by Mr William Anderson; on "Secondary Batteries," by Mr Preece; on "Automatic Selling Machines," by Mr. J. G. Lorrain; on "Arc Lamps and their Mechanism," by Professor Silvanus Thompson; on the "Irish Lace Industry," by Mr. Alan Cole; and on the "Use of Spirit as an Agent in prime Movers," by Mr. A. F. Yarrow.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Science and Art Department.—Mr. W. E. Youle, in answer to the query of "Student" ("Science and Art Department"), advises examination of filtrate "after separation of the inorganic bases *as usual*," that the organic acids may be detected in it. What is the *usual* method of separation pursued? If it involves (1) use of hot acids or mixtures of acids to effect solution, (2) concentration with HNO_3 and gentle ignition to ensure peroxidation of Fe, &c., (3) complete ignition preceeding separation of alkalies, it is to be feared that the amount of unaltered organic matter surviving for "Student's" examination will be small indeed. May I suggest the adoption of the, to me, usual method of decomposing original solution with excess of sodic carbonate, and examining the filtrate—after neutralisation by acids appropriate to test to be applied—for acids organic or inorganic (if required to be determined)? If difficulty occurs, owing to incomplete precipitation of metals by $NaCO_3$ in presence of organic acids, the accurate and careful method recommended by Fresenius ("Qualitative Analysis," 10th English Edition, from 15th German Edition, pp. 325 and 281) should be followed. "Student should pay great attention to odours evolved by the organic acids and their salts when subjected to destructive distillation in a hard glass tube, and observe closely the effect of warming with dilute and concentrated hydric sulphate.—W. Popplewell Bloxam.

MEETINGS FOR THE WEEK

Monday, 14th.—Medical, 8.30.
Tuesday, 14th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
Wednesday, 16th.—Society of Arts, 8. "The Channel Tunnel," by Colonel Hozier.
—— Meteorological, 7. (Anniversary).
Thursday, 17th.—Royal, 4.30.
—— Chemical, 8. "On a Cubical Form of Bismuthous Oxide," by M. M. P. Muir and Arthur Hutchinson. "On the Iodides of Copper," by Douglas Carnegie. "On the Periodates: No. II.," by C. W. Kimmins. "On Compounds of Arsenious Oxide and Antimonious Oxide with Sulphuric Anhydride," by R. H. Adie. "On a Compound of Boron Oxide with Sulphuric Anhydride," by R. F. Davey.

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THE CHEMICAL NEWS.

VOL. LIX. No. 1521.

ON THE

ESTIMATION OF TITANIUM IN NATURAL SILICATES.

By PHILIP HOLLAND.

As it is often necessary in the analytical course for silicates to take account of the titanic oxide, since it occurs in some rocks in notable amount, it may be useful to give the details of a few experiments lately made on the commonly accepted plan of separating titanic oxide from the oxides of iron and aluminium.

A pure specimen of TiO_2 was prepared in the first place by converting the commercial article into potassic fluo-titanate. This, after several crystallisations, was decomposed by ammonia, and the product well washed and ignited. So made from a fairly pure commercial sample, the titanic dioxide was found free from aluminium and iron. On ignition it became yellow, but regained its original perfect whiteness when cold.

As the practice of decomposing silicates by HF in the presence of H_2SO_4 is now more common than formerly, it was desirable to learn if titanic oxide is quite stable under these conditions, for as Riley has shown (*Journal of the Chemical Society*, xii., 13) there is considerable loss in the absence of oil of vitriol. Another point, bearing directly on the estimation of titanic oxide, was the conditions of complete precipitation when the solution of a bisulphate fusion of such oxide is boiled, this being a method much in vogue for parting titanic oxide from the oxides of aluminium and iron.

To settle the first question, viz., the fixity of titanic oxide when digested with HF and a little H_2SO_4, a few experiments were made as follows:—

Into a weighed platinum crucible, already containing a known weight of recently ignited titanic oxide, was put 2 c.c. of a dilute H_2SO_4, to be presently described. Next was added, at three stages, as much re-distilled HF (not the commercial article) as in a blank trial sufficed to volatilise 1 grm. of pure silica. After each addition of the acid the contents of the covered crucible were carried to dryness, and, before weighing, ignited, at first gently and then strongly with the blast-lamp. Below are the weights of the TiO_2 before and after the treatment:—

Wt. of TiO_2.	Wt. after treatment.	Error.
Grms.	Grms.	
0·0340	0·0340	—
0·0414	0·0413	0·0001
0·0520	0·0520	—
0·0352	0·0352	—

There appears to be no loss in the presence of vitriol. In the absence of vitriol, however, a single experiment made on 0·0466 grm. gave, after treatment, 0·0340 grm. as the weight of the residue, showing a loss of 25·3 per cent of the TiO_2 taken. In this experiment the oxide was only once treated with HF before ignition. Further treatments in the same way would obviously have removed the whole.

Passing now to the complete separation of titanic oxide by boiling the acid solution of the bisulphate fusion, the fact is well known that incomplete separation attends the use of too much free mineral acid. My own experiments confirm those of Gooch and others in this respect.

For the test experiments to show the plan of separating titanic oxide from iron and aluminium the following solutions were made up:—

(*a*). Dilute acid, of which 5 c.c. contained 0·8 grm. of SO_3.

(*b*). Solution of ferrous sulphate and potash alum, of which 100 c.c. contained alum equal to 0·26 grm. Al_2O_3, and iron salt equal to 0·026 grm. of Fe_2O_3.

(*c*). Solution of titanic oxide (made by fusing TiO_2 with potassium acid sulphate), of which 100 c.c. contained 10 m.grms. of TiO_2.

Solution "*b*" was assumed to represent per 100 c.c. the weight of $Al_2O_3 + Fe_2O_3$ extracted from 1 grm. of an average fire-clay that had been subjected to the fluoric treatment. The dilute acid "*a*" contained in 5 c.c. rather more than sufficient SO_3 to combine with the 0·286 grms. of the mixed oxides present in 100 c.c. of solution "*b*."

In the experiment to be now described 100 c.c. of "*b*" was made *just* alkaline with ammonia, 5 c.c. of "*a*" was next added, as also 50 c.c. of a saturated solution of SO_2, and finally boiling water till the vol. was about 900 c.c. On boiling the contents of the covered beaker for twenty minutes the solution remained perfectly clear. In the next place an addition of 10 c.c. of "*c*" was made equal to 1 m.grm. of TiO_2 and the boiling continued for twenty minutes longer. This addition did not appear to cause any change, still, on allowing the beaker to stand for twelve hours still covered, it was easy on decanting nearly all the fluid, to see a slight opalescence in what remained when this was shaken round. I assume the opalescence to have been due to titanic oxide, since it did not disappear on adding more acid, as it should have done if caused by basic aluminium sulphate. This experiment afforded then some evidence as to the conditions favourable to the precipitation of small amounts of titanic oxide.

In the next four experiments 100 c.c. of "*b*" and the same of "*c*" were mixed, made just alkaline as before, re-acidified with 5 c.c. of "*a*" and 50 c.c. of solution of SO_2 in the order given. The whole, further diluted to 900 c.c. with boiling water, was boiled for twenty minutes. The collected precipitates, when washed, ignited, and weighed, were in all cases slightly coloured. They were therefore fused with bisulphate and the precipitation repeated. In the third column are the results of this treatment.

TiO_2 taken.	First Precipitation.	Second Precipitation.
10 m.grms.	9·8 m.grms.	9·0 m.grms.
,,	11·1 ,,	8·8 ,,
,,	10·3 ,,	9·6 ,,
,,	10·0 ,,	8·9 ,,

A further experiment was made as before, taking, however, 200 c.c. of the titanic solution, equal to 20 m.grms. TiO_2. The numbers were:—

1st precipitation	20·2 m.grms.
2nd , ...	19·7 ,,

The titanic oxide, after the second precipitation and ignition, was not *absolutely* white, thus showing the tendency the precipitate has to carry down iron and doubtless alumina also.

I will now give in outline a scheme, with an example of the analysis of a silicate to which a known weight of titanic oxide was added. The rock chosen was granite, the specimen being part of a drift boulder from the Ribble Docks excavation at Preston. A qualitative analysis proved it to contain TiO_2, CaO, and MgO, in addition to the usual constituents of granite. The TiO_2 amounted to 0·62 per cent. Now, as some basalts contain 3 per cent and more of TiO_2, and as I had recently met with 1·94 per cent in a specimen of igneous rock from the Isle of Man, it seemed enough for the purposes of the test experiments to make up an artificial sample by adding to the granite a known additional weight of TiO_2. The rock was powdered, ignited, and sifted through fine muslin, and the TiO_2, also in fine powder, was added to the extent of 3 per cent over and above that already in the sample. The mixing of the TiO_2 with the silicate was done in a

dry and warm wide-mouthed bottle. After mixing, the sample was gently ignited and put in a closed tube ready for work. The plan of analysis was this. Into a somewhat large platinum crucible was put 2 grms. of the sample, which was then moistened throughout with dilute H_2SO_4, a little re-distilled HF was next added, and the mixing promoted by careful shaking. As much heat is evolved when silicates are treated with strong solution of HF, often causing violent effervescence; this acid should be added by degrees. When 5 grms. or so had been added, the crucible covered with its lid was heated in an air-bath of the following construction, which has been found convenient for such operations. It consists of a moderately thick unglazed iron dish of 20 c.m. diameter, with a cone-shaped sheet-iron cover open at top and bottom, and serrated at its bottom and wider end, which rests just inside the dish when in use. The cover, 16 c.m. high and 9 c.m. diameter at its apex, has projecting slips at two sides which serve as handles. A few stout wire tripods of different heights and some porcelain triangles support crucible dishes, &c., whilst a clamp at the top of the cover carries a thermometer whenever this is required. Two such air-baths were made for me some time ago, which appear to answer all the purposes of the more costly forms, usually of copper.

To return to the analysis. The air-bath was heated to about 100° C., when the thermometer was removed and the crucible or crucibles, for two can be heated at one time, were placed on one of the supports; as the operation progressed, the temperature of the bath was raised until the residues appeared dry. At this stage concentrated HCl was added and the crucibles heated anew. Provided enough HF had been used in the first instance, the residues dissolved with the exception of a little TiO_2. Any undissolved TiO_2 was caught on a filter, washed, and the filtrate collected in a half-litre flask, in which it was oxidised by a few drops of chlorine-water. The small filter and residue were ignited, fused with a little bisulphate, and the solution of the fusion, after filtration, added to the contents of the flask, which were now diluted to the mark, mixed, and divided into portions D and E.

Portion D, = 1 grm. of sample, was diluted somewhat, and in it were the Al_2O_3, Fe_2O_3, and TiO_2, co-precipitated by the ammonium acetate plan, repeating the operation and uniting the two filtrates for the MnO, CaO, and MgO estimations. Before, however, proceeding to separate these, the united filtrate was treated for a little Al_2O_3 it frequently contained, which was weighed along with the major portion in the mixed precipitate. The latter, after weighing, was finely powdered, collected in a tared platinum crucible to learn its proportion to the whole, and fused with recently ignited bisulphate. The fusion, if properly managed by carefully rotating the crucible over the flame, should be quite clear and free from suspended particles of TiO_2 or undissolved bases. The fusion was next quickly extracted at 80° C. with water containing a little vitriol, transferred to a large beaker, and treated with ammonia, &c., just as in the earlier experiments. At the end of the twenty minutes' boiling the solution was filtered and the precipitate, after drying and igniting, fused afresh, repeating the remaining operations as above, before final weighing. Turning to portion E of the original solution: in it, the iron precipitated first by ammonium sulphide in the presence of the tartrate was washed, re-dissolved in HCl, oxidised, and re-precipitated as ferric oxide by ammonia.

It will be observed the scheme so far has given the united weights of the $Al_2O_3+Fe_2O_3+TiO_2$, as also the weight of the TiO_2 and that of the Fe_2O_3. The Al_2O_3 was estimated by difference. As regards the silica and alkalies, these were estimated on fresh portions of the original sample; the alkalies by Smith's lime fusion plan.

The following are the numbers for the several constituents of the sample, which was analysed precisely in the way described. The TiO_2 assumed to be present was 3·62 per cent:—

	1.	2.	3.	4.	Mean.
SiO_2 ..	65·62	65·48			65·550
Al_2O_3. ..	17·57	17·21	17·32	17·43	17·382
Fe_2O_3 ..	4·64	5·08	4·76	4·82	4·825
TiO_2 . ..	3·47	3·52	3·58	3·49	3·515
MnO . ..	0·18	0·23			0·205
CaO . ..	0·12				0·120
MgO . ..	0·10				0·100
K_2O.. ..	5·73	5·75			5·740
Na_2O. ..	2·66	2·50			2·580
					100·017

Before closing this paper I would call attention to a plan of separating titanic oxide from alumina and ferric oxide, ascribed to G. Roussel at p. 113 of "Select Methods in Chemical Analysis." He takes the acid solution containing them and adds solution of SO_2, sodium sulphate, and thiosulphate, and boils. By this means the alumina and titanic oxide are thrown down, ferrous iron remaining in solution. The mixed precipitate containing sulphur is washed, gently heated to drive off sulphur, and then digested in a sealed tube with hot concentrated HCl, which extracts the Al_2O_3, leaving the TiO_2 sufficiently pure to wash, ignite, and weigh. The process failed in my hands. It was tried on 1 grm. of the silicate sample, when the numbers were:—

	Per cent.
TiO_2 undissolved by the HCl	2·27
,, recovered from the acid	1·27
	3·54

As ignited TiO_2, *per se*, is insoluble in hot HCl, I attributed the failure to the fact that in driving off the sulphur by heat some of the TiO_2 had combined with the Al_2O_3 to form a titanate which dissolved in strong HCl, just as some natural titanates are known to do.

In support of the hypothesis that combination might have occurred from heating the oxides too strongly, I took 0·1415 grm. of Al_2O_3, 0·0834 grm. Fe_2O_3, and 0·0382 grm. of TiO_2. The two first were disssolved in HCl and the TiO_2 in water after fusion with bisulphate. To the mixed solutions ammonia was added in not too great excess, and the whole boiled. The resulting precipitate was then collected, washed, and *ignited*. It was next powdered and digested with HCl at 100° C. in a sealed tube, when the whole dissolved with the exception of 3·8 m.grms., showing that over 90 per cent of the TiO_2 had passed into solution. In carrying out Roussel's process, wherein success may depend on the temperature at which the sulphur is expelled, it would appear preferable to extract the latter with CS_2 and then treat the residue with HCl to remove Al_2O_3, or better perhaps with dilute H_2SO_4, which would be less likely to dissolve any TiO_2.

The method of full analysis here set out has given good results for granites, basalts, felstones, and the like. Where, however, a qualitative examination reveals P_2O_5 and TiO_2, a somewhat different course for the separation of the TiO_2 must be pursued, for, as Blair has shown, each one of these two, when both are associated in a mineral, interferes with the correct estimation of the other, owing to formation of titanic phosphate.

In silicates where ferrous iron occurs this is found by digesting in a sealed tube, at 120° C., 2 to 4 grms. of the rock in fine powder with chlorine-free HCl. The solution is titrated with bichromate. The more accurate plan is to treat the silicate with HF, in which the SO_2 present in commercial samples has been first oxidised by permanganate, carrying out the extraction in the way recommended by Fresenius.

From the foregoing experiments it will be seen that but relatively small weights of TiO_2 have been taken. It was found easier to obain aluminium and iron-free precipitates when the weight of titanic oxide was only 2 to 5 centigrms. than when it reached 1 to 1·5 decigrms. There is no difficulty in recovering small amounts of TiO_2

from the beaker in which the precipitation is made, provided a little concentrated HCl be heated in it for a short time. This, though it does not always entirely dissolve the strongly adherent oxide, so far loosens it as to allow of its recovery with the feather. Any TiO_2 dissolved in the acid is thrown down by ammonia.

DECOMPOSITION OF NICKEL AND COBALT.

The Vienna correspondent of the *Times*, telegraphing on the 14th inst., says that Dr. Krüss, the well-known chemist, of Munich, has succeeded in decomposing the metals cobalt and nickel, hitherto believed to be elements. He finds that both metals have one constituent in common, and one in which they differ.

[We hope to give further particulars in our next number.—*Ed.* C. N.]

THE PHYSICAL PROPERTIES OF THE GRAPHITES OBTAINED FROM VARIOUS METALS AFTER THE SEPARATION OF THE SAME BY MEANS OF DILUTE ACIDS.

By H. N. WARREN, Research Analyst.

The metals of the third group, and especially iron, undoubtedly furnish graphite most readily when maintained at an elevated temperature in contact with carbon; the scales thus separated from the cast metal being possessed of larger magnitude than those obtainable from either nickel or cobalt, both these metals producing graphite of a much finer quality, and in many instances, unless viewed by the aid of a microscope, being indistinguishable from lamp-black, while in all other respects both their varieties closely resemble each other. But on further following the group to manganese, a considerable variance is observed; for on dissolving a portion of ferromanganese containing a high percentage of that metal, a graphite is obtained consisting of much thinner scales than by similarly treating cast-iron, and possessed of a distinct brownish tint, being at the same time less readily oxidised. Further, if commercial black oxide of manganese be reduced by means of carbon at a high temperature, and the metallic manganese thus obtained be dissolved by the aid of dilute acids, a graphite is produced presenting a perfectly brown colour, the dimension of the scales being somewhat considerable. I have also frequently observed, after carefully selecting the same, that several of the scales appear decidedly translucent and still less combustible than that obtainable from ferromanganese. Chromeisen thus treated usually gives much brighter scales, and at the same time harder, than those obtainable in the case of iron, whereas those produced by the dissolution of cast chromium in appearance approach more closely to silicon, being entirely destitute of any brownish tinge and possessing a semi-metallic lustre, being less energetic to combine with oxygen, unless when heated in a current of the pure gas.

The above mentioned graphites thus produced may be undoubtedly influenced by the difference of the fusion points of the various metals employed for their production; thus, for instance, chromium being the most difficult of fusion tends to produce a graphite possessing a more stable form than that produced by either iron, nickel, or cobalt. Strange to say, however, each modification may be inverted in the same manner as silicon behaves towards allotropy; thus, if a small quantity of pure iron be maintained in the liquid form by the aid of an oxhydrogen flame, and a quantity of the brown modification obtained by treating manganese with dilute acids be introduced into the liquid iron, and the graphite afterwards separated in the usual manner, it will be found on examination to correspond in every respect with the graphite usually produced by such means.

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SPECTRUM ANALYSIS OF CADMIUM.*

By A. GRÜNWALD,
Professor of Mathematics in the Imp. Roy. German Polytechnic University at Prague.

(Concluded from p. 19).

Conclusion.

(1.) I have hitherto principally used the water spectrum as comparison spectrum, because it is now known with great accuracy and to a large extent.

The probable errors of its wave-lengths, measured by Liveing and Dewar, may ordinarily amount (according to the observers) to from 0·2 to 0·3; but in very weak and also in diffuse or broad lines the errors may be greater, and the most part of the nebulous lines may be in reality only representatives of double or even more lines. A similar thing may be the case with regard to the wave-lengths of the ultra violet rays of the so-called elements measured by Hartley and Adeney, and by Liveing and Dewar. (It would be, however, very desirable for the sake of control, that these excellent observers and other observers equally qualified, should repeat all these measurements with the aid of Rowland's method by concave gratings, which is evidently simpler and less liable to errors than that hitherto employed, as it substitutes linear for angular measurements, and secures therewith the greatest possible exactness).

As the lines of the water spectrum lie close together, the doubt arises whether the coincidences or close agreements between the lines calculated and the corresponding lines of the water-spectrum may not be perhaps only accidental and not real. For the closer set the lines of a comparison spectrum (for instance of the solar spectrum, or as here of the water spectrum), the easier it can happen that some wave-lengths written (or lines delineated) at random may agree with more or less accuracy with wave-lengths or lines of the compared spectrum, and that the conclusions founded upon such comparisons may lose their demonstrating power and prove nothing.

If this doubt, which I have already apprehended and kept in view from the beginning of my researches, were to be admitted without any restriction, if there were no means or criteria proper to distinguish pretended or accidental from well-founded and real coincidences, or close agreements—

(α.) Between one set of rays observed and other observed rays.

(β.) Between calculated and observed wave-lengths.

(γ.) Between two sets of wave-lengths derived by calculation from two distinct sets of directly observed wave-lengths.

If that be so, the trouble and care applied to the accurate measurements of certain spectra, such as the solar spectrum or the water spectrum, would be truly foolish, or at least superfluous, as no one could make use of the result for anything. Nay, what is more, if we keep in view that even the spectra of such elements as seem to emit only few and often far distant rays, may be probably merely incomplete representatives of the true spectra which may (at least in certain regions) consist of close set but very faint and, therefore, ordinarily not visible lines, it would have to be conceded that almost the whole

* A Paper read before the Royal Society, December 13, 1888.

use of spectrum analysis, so much praised, would be an illusion.

Fortunately this is not the case, and even my researches furnish already, and will supply in future, still more remedies (criteria), proper to remove the doubt above mentioned, and to distinguish real agreements (even of few lines) with great probability from others only accidental.

As the evidence of laws in physics rests upon the testimony of coincidences or close agreements, either (α) between two series of direct measurements or observed images (for instance, of spectral lines), or (β) between numbers calculated from one series of observations and a series of direct measurements, or, finally (γ), between two series of numbers derived by calculation according to certain rules from two different series of direct measurements, it is plain that the reality or probability of a given series of such agreements can be proved by other series of agreements connected with the former by laws established and ascertained beforehand. The more such series of coincidences or agreements ("criteria") co-ordinated to the series of agreements to be tested are satisfied, the greater is the probability that the series tested is not an accidental one, but consists rather of real agreements.

When such series (co-ordinated by certain laws as criteria to a series under examination) are not known, as is, for instance, the case in the first examination of agreements, which are themselves to be used as criteria for others, and when numerous series of agreements of a similar kind are possible, the evidence that no better series of agreements of the same kind exists, may in the first instance warrant sufficiently the probability of the series under examination. Particularly striking, however, would the evidence become if the close agreements under examination could be transformed into complete coincidences by minimum corrections applied to the compared numbers within the limits of possible errors, and if the values thus corrected should be confirmed by later and more accurate measurements, *experimentum crucis!* (crucial proof!)

Finally, the calculus of probabilities may also afford us its assistance in the case when the series under examination consists of numerous single agreements, and may convince us, upon the ground of the known observations, of the degree of probability for the real and not accidental character of the examined agreements. Especially may the graphical method be used with advantage, given by E. F. J. Love (now Lecturer in the University of Melbourne, Australia). (See the interesting paper of Love "On a Method of Discriminating Real from Accidental Coincidences between the Lines of different Spectra, with some Applications;" communicated to the Physical Society—read November 26th, 1887—in the *Philosophical Magazine*, 1888, pp. 1—6).

(2.) In order to determine the rational numbers occurring in the criteria used, I was compelled to multiply the simple wave-lengths of the rays of hydrogen and oxygen with the rational numbers $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{5}$, &c., and to compare the results with the wave-lengths of the water spectrum with one another. I searched at once by chain division for rational rhythmical relations between the wave-lengths of the compared spectra, and tried then the rational numbers thus found on other wave-lengths to prove if they were or were not reduction factors for certain groups of the latter.

In so far as only a few rational reduction factors were the outcome of a great number of such mathematical experiments, in spite of the nearness to one another of the lines due to the water spectrum, and in so far as the above-mentioned calculations, originally performed with a very incomplete water spectrum,—were later brilliantly confirmed and amplified by the later new and more accurate measurements, communicated to me by Mr. G. D. Liveing, all possible security was given at first that the few found rational numbers were not accidental, but rather characteristic or typical of the relations between the compared spectra. Their internal meanings result from theoretical reflections which belong to the first elements of new chemical mechanics, and will form the last, but perhaps not the least interesting, part of my spectral analytical communications.

As soon as the criteria that characterise the condensation forms of the primary bodies occurring in hydrogen, oxygen, and in aqueous vapour were established and ascertained, the possibility was afforded of admitting and ultimately recognising the correspondence of certain rays in the spectra of given elements with certain condensation forms of the primary elements, or of making such relations at least very probable. For suppose the agreements corresponding to a single criterion to be for some rays only accidental, there would be little probability that the same rays would satisfy simultaneously also a second criterion, and much less probability that they would answer to a third or even to a fourth criterion with the same accuracy. The greatest difference admissible between two compared numbers whose probable errors may be numerically δ and δ' respectively, is δ and δ' (numerically); this will be 0·4 to 0·6, if the errors δ and δ' amount to 0·2 to 0·3, as may be the case for a great part of my comparisons.

Hence there is, I believe, sufficient security given for the exactness of the spectrum analyses performed in such a manner, if not in all single cases, at least for the result as a whole; a security which could only be augmented by new and more accurate measurements, in so far as these would produce better agreements between the compared numbers.

(3.) The rhythmical relations which exist between the wave-lengths, due to the condensation forms of the primary bodies and between the hydrogen or the oxygen spectrum, can be used at present only in a few cases as criteria. In the remaining cases they give rise to wave-lengths still unknown, due to such condensation forms of the primary elements, such as occur in hydrogen or in oxygen, and in peculiar physical modifications also in other secondary elements. The wave-lengths thus obtained form not only important supplements to the wave lengths of the same kind hitherto observed, but supply also at once handles for the experimental investigation of my theory, in so far as the corresponding rays can really be found partly in the spectra of hydrogen or of oxygen, partly in the spectra of such bodies as contain the condensation forms referred to in proper physical modifications. (See the Introduction, sub. III.)

The statement, however, that rays due to a special condensation form of a primary element which in a certain physical modification disappear on account of their extremely low or vanishing intensity, may be seen (or made visible by the photographic plate) in another physical modification of the same chemical condensation form, and *vice versâ*, is by no means an hypothesis, but rather the expression of a mechanical necessity.

(4.) The experimental and theoretical spectrum analysis in the largest sense is a field in which chemistry, physics, and astronomy (astrophysics) touch one another intimately. As such it forms a central or nodal point of the whole field of our perception and knowledge.

This position leads naturally to the conclusion that as every important progress upon that ground results from the co-operation of the sciences above mentioned, so every new discovery upon that field reacts simultaneously upon chemistry, physics, and astronomy.

For mathematics, which has for its object to penetrate natural philosophy, especially in the more concrete form of mechanics, acquires on that ground the office of disposing of the almost overwhelming abundance of important physical and chemical constants (principally wave-lengths), which experimental investigations supply in order to search for and to find the secret relations hidden in that ocean of numbers, and to discover the internal mechanical meaning of the latter.

Here is the foundation upon which I base my re-

searches: to this belong the mathematical experiments, the troublesome calculation by which I, at first groping about entirely in the dark, then seeing more and more clearly, have brought to light a small part of the numerical relations concealed in the large amount of material of measured wave-lengths: to this the dynamical researches by which I have tried to open up, with the aid of a minimum of most probable hypotheses, the path to the gradual understanding of their internal meanings.

Whatever may be the final fate of my results in this matter, whether they be or be not accepted by the chemists of our days, they merit at least to be regarded with attention and to be examined without prejudice. I am, for my part, thoroughly convinced that my results in that field, and especially the chief result of all my relative researches, "that many, perhaps all, bodies hitherto considered as elements are compounds composed of condensation forms of the primary elements '*a*' and '*b*' of hydrogen $H = ba_4$ in various physical modifications," will be finally acknowledged and received as true or at least as most probable.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Continued from p. 23).

Criticism of Wollny's Methods.

Goldmann criticises Wollny's original method chiefly because it gives only a part of the volatile acid present and takes no account of the whole. It has never been claimed, however, for the Reichert process that it gave anything more than a portion of the volatile acid present, but the percentage of the total volatile acids obtained is approximately constant, and therefore the results are comparable among themselves.

Goldmann proposes to remove the last traces of alcohol after saponification by distillation in a current of steam. Before the distillation of any part of the alcohol, however, the solution is heated with a reflux condenser for half an hour so that any ethers which have been formed may be re-combined by the excess of alkali present. The apparatus for the removal of the last traces of alcohol is illustrated in the *Chemiker Zeitung*, No. 14, 1888, p. 216.

Goldmann's paper is so long that for all details I can only refer to the original. The method finally adopted by him is as follows:—5 grms. of the melted butter fat are weighed in a flask of 300 c.c. capacity, the neck of which is 12 c.m. long and 2 c.m. wide. Add 10 c.c. alcohol, 96 per cent, and 2 c.c. of a 50 per cent aqueous soda lye made and preserved out of contact with carbonic acid. The flask, furnished with a reflux condenser, is heated for twenty minutes with a small flame. The condenser is turned to an angle of 55°, and 6 c.c. of the alcohol distilled off. The flame is then extinguished, the apparatus connected with the flask delivering steam, and the whole of the alcohol driven off by a slow current of steam.

Full directions for the conduct of this part of the work are given by Goldmann.

After the alcohol is driven off the soap is decomposed by the addition of 5 c.c. of sulphuric acid containing 200 c.c. of strong acid to the litre. The volatile acids are distilled off in a current of steam and 600 c.c. of distillate taken, which is titrated with one-tenth normal solution of barium hydrate.—(Abstract from *Chemiker Zeitung*, 1888, No. 12, p. 183; No. 14, p. 216; No. 20, p. 317).

Application of the Reichert-Meissl-Wollny Method to Italian Butters.

Besana has made an extended examination of 114 samples of butter, and from the study of them draws the following conclusions:—

One hundred and fourteen samples of butter examined belong to 30 provinces. These show a melting-point from a minimum of 33° C. to a maximum of 37·7°, not including one sample which seems to be essentially different in constitution. No positive relation has been established between the point of fusion and the quantity of volatile acids; therefore the knowledge of the first offers no special utility.

The percentage of volatile acids, or the quantity of the same expressed in c.c. of deci-normal alkaline solutions, shows a variation from a minimum of 21·83 to a maximum of 30·19. The classification of the 114 samples of butter, according to their quality or condition, would be as follows:—

Volatile acids from		No. of Samples.
29	to 30·19	23
28	to 29	25
27	to 28	49
26	to 27	9
25	to 26	3
24	to 25	2
23	to 24	1
21·80	to 22	2
		114

The variation in the quantity of the volatile acids, in the different butters, already recognised by various experimenters in Germany and Sweden, is confirmed by these researches also in the Italian butters. Even the butters of the same dairy may present quite different qualities, although made within a very few days of each other. Upon the cause of this variability I have not ventured, up to the present time, to present any theory, and I have not even sufficient data for the support or contradiction of the theories of others. I hold the causes to be biological, and I would like the researches tending to their discovery to be made by following very closely the chemistry of nutrition and of the lacteal secretions or the transformation of aliment into milk, keeping note of the quantity and quality of the food, the stage of lactation, the condition of health in the animal, &c.; but such researches, in my opinion, should be followed upon individual cases, instead of upon a group of milch cows.—(Prof. Carlo Besana, extract from the journal *Le Stazioni Sperimentali Agrarie Italiane*, 1888, vol. xiv).

In regard to the cost of the lactocrite, I would say that I recently secured one for the West Virginia Experiment Station for 125 dollars from the De Laval Separator Company, of Philadelphia.

It is arranged in such a way that it can be set in the place of the drum of the separator, and run by the power that runs the latter. The construction is very simple, and for the rapid testing of milk it appears to be the most satisfactory method yet devised.

There is likewise an apparatus provided by the same company which is intended to mix artificial fats with the skimmed milk. It is arranged so that the liquid fat and the skimmed milk are violently whipped together, the fat being delivered in a finely divided condition.

I have been suspicious for a considerable time that much of the cream now in the market is cream manufactured in this or some similar manner, and, as we have ordered one of these machines for the experiment station, we propose in the near future to see to what extent we can mix fat of cotton, pig, or cow, with skimmed milk to supply the gastronomic needs of our national capital.

Mr. Richards spoke of Swedish machines for taking out cream and putting back cotton-seed oil, illustrated in the London *Engineering*

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

The Secretary then read the following communication from Professor G. E. Patrick, of Iowa:—

Notes on the Method for Soluble and Insoluble Fat Acids.

In the determination of soluble and insoluble fat acids I have recently found it convenient, as well as economical of time and material, to change slightly the mode of procedure as laid down in the method (originally Muter's) adopted by this Association at its last meeting (1887), and published in *Bulletin* No. 16 from the Department of Agriculture, Chemical Division, pp. 70 and 71.

The purpose of the modification is to avoid the use of a separate saponifying bottle, and the consequent transfer of the soap solution to an Erlenmeyer flask, and evaporation of the alcohol added in this transfer.

This end is accomplished by saponifying directly in the Erlenmeyer, the latter (with stopper tied down) being inclosed in a "conversion" jar with tight cover, and containing absolute alcohol (50 c.c.), the vapour of which gives an outside pressure on the Erlenmeyer equal to that within. The jar is made with vertical sides, and is only a little larger than the flask it is to inclose; its cover is held down by a screw-clamp in the usual way, a disc or washer of rubber making the union tight.

Breakage by contact of the flask with the walls of the jar while agitating is prevented by a ring of corks strung upon a wire. Thus arranged, *with a tight jar*, there is no danger of breaking the Erlenmeyer if the work is executed with ordinary care. Fifty c.c. of absolute alcohol in the jar will suffice for many analyses.

Two styles of jar have been tried, one of heavy glass, iron bound (made by Eimer Amend), the other of heavy sheet copper, made (excepting the clamp) by an ordinary tinsmith; the cover of each is a thick ground-glass plate, with a metal disc to receive the pressure of the screw. The glass one, allowing a view of the interior during saponification, is the more convenient.

The saponification is conducted in a steam or air oven at a few degrees below 100 c.m. Neither style of jar can be heated directly on the water or steam *bath* with safety to the contents. This needs further trial.

Another slight deviation from the method of last year, which I find convenient, is to retain the cake of insoluble acids in the Erlenmeyer for weighing, using alcohol merely to dissolve into the flask whatever fat acids are on the dried filter. This small amount of alcohol is quickly removed, first on the water-bath and then in the oven, with a current of dry air or hydrogen.

By these two changes in the method the entire determination of insoluble acids is effected without any transfer of material from first to last. At the start the filtered, still liquid, and well-shaken fat is weighed into the tared Erlenmeyer; at the end, after the insoluble acids are weighed, they are removed, and the flask is dried and tared again to insure against error from "nicking" or corrosion during the operation. However, in the few trials thus far made, the first and last weights of the flask have been practically identical.

Report of the Committee on Phosphoric Acid.

As required by the constitution of the Association, the Committee on Phosphoric Acid herewith presents its report. The report presents: 1, brief notices of new analytical methods for determining phosphoric acid proposed during the year; 2, results of work done by the committee and members of the Association; 3, recommendations for the next year.

C. Mohr (*Chem. Zeit.*, 11, 417—418; Abs. *J. Chem. Soc.*, 1887, p. 884) proposes the following volumetric method for phosphoric acid:—Two grms. of the phosphatic substance is treated with successive small quantities of 2 per cent sulphuric acid in a mortar. The residue is added to the extracts, and the whole made up to 100 c.c. and allowed to digest for one hour; 10 c.c. of the filtered solution, corresponding to 0·2 grm., are then treated with potassium ferrocyanide so long as iron is precipitated. After the addition of sodium acetate, the phosphoric acid is titrated in the usual way with a standard solution of uranium acetate. It is stated that the end reaction is not influenced either by an excess of potassium ferrocyanide or by the presence of Prussian blue.

G. Kennepohl (*Chem. Zeit.*, 11, 1089-1091; Abs. *J. Chem. Soc.*, 1888, 321; *J. Soc. Chem. Ind.*, 6, 680) confirms the opinion expressed by Klein (*Chem. Zeit.*, 10, 721; *J. Chem. Soc.*, 1886, 835) as to the practical non-occurrence of iron phosphide in normal Thomas slag. The phosphoric acid may be accurately determined in the following manner: Ten grms. of the finely powdered slag are introduced into a 500 c.c. flask, moistened with alcohol to prevent adhesion, and heated in a water bath for at least half an hour with 40 c.c. of HCl (1·12 sp. gr.) and 40 c.c. of water. After cooling the flask is filled to the graduation mark and the solution filtered. An aliquot part is mixed with ammonium nitrate and molybdic solution without previous removal of the silica. The solution, after heating at about 80° for fifteen minutes, is filtered, and the precipitate washed with water containing 3 per cent of nitric acid, re-dissolved in 2½ per cent ammonia, and then precipitated with magnesia mixture. The presence of silica does not interfere, owing to the ready solubility of ammonium silico-molybdate in the washing water.

If the presence of ferrous salts should tend to cause the separation of molybdic oxide, which dissolves but slowly in ammonia, an addition of nitric acid or bromine, before adding the molybdic solution, will insure the production of a precipitate instantaneously soluble in the ammonia.

Isbert and Stutzer (*Zeit. Anal. Chem.*, 26, 583-587; Abs. *J. Chem. Soc.*, 1888, 194; Chem. News, 57, 211; *J. Soc. Chem. Ind.*, 7, 44; *J. Anal. Chem.*, 2, 193). The method based on the determination of the ammonia in the phospho-molybdate precipitate (*Chem. Zeit.*, 11, 223) is confirmed. A further simplification consists in washing the yellow precipitate with cold water, instead of with ammonium nitrate solution. The ammonium silico-molybdate is soluble in pure cold water, although insoluble in ammonium nitrate solution. On the other hand, the phospho-molybdate requires 10,000 parts of cold water for its solution.

The analysis is conducted as follows:—

Five grms. of the phosphate are dissolved in hydrochloric acid or aqua-regia, diluted to 500 c.c. and filtered. Fifty centimetres of the filtrate are mixed with an excess of ammonia, acidulated with nitric acid, and the phosphoric acid precipitated with ammonium molybdate. The precipitate is allowed to settle at 60° to 70° C. for fifteen minutes, and then filtered, the supernatant liquid being first passed through the filter, the precipitate repeatedly washed by decantation, then placed upon the filter and washed with water until the wash water amounts to about 250 c.c. The precipitate is transferred, filter and all, to a ¾-litre Erlenmeyer flask, sodium hydroxide added in excess, and the ammonia distilled off into a solution of standard acid, which is then titrated back with baryta water, using rosolic acid as the indicator.

One part of nitrogen in the precipitate corresponds with 1·654 parts of phosphoric acid.

Test analyses with known quantities of phosphate, with and without silicic acid, and comparative tests of phosphatic manures by the above and gravimetric process, show that for commercial purposes the method is sufficiently accurate.

Ch. Malot (*Monit. Scient.*, 1887, 487; *J. Pharm.*, 16, 157-159; *J. Chem. Soc.*, 1887, 1063; *J. Soc. Chem. Ind.*, 6, 563) describes a new volumetric method for P_2O_5 by uranium nitrate. Oxide of uranium gives a green lake with cochineal, which property is utilised for the determination of phosphoric acid.

The phosphate is treated according to Joulie's method,

i.e., dissolved in HCl, the phosphoric acid precipitated with citro-magnesium mixture, and the precipitate dissolved in dilute nitric acid. A few drops of tincture of cochineal are added, then ammonia until the violet colouration just appears, and this in its turn is made to disappear with one or two drops of nitric acid. The solution is now heated to 100° C., 5 c.c. of sodium acetate solution added, and mixture titrated with uranium nitrate. Each drop of the latter causes a greenish-blue zone, which, on agitation, disappears again. As soon as precipitation is complete, the solution assumes a lasting greenish-blue colour, remaining unchanged by excess of the uranium solution. The end reaction is most distinct. By employing a very dilute solution of uranium nitrate, the determination is rendered very exact. The author uses solutions, 1 c.c. of which represents 0·001 grm. of phosphoric acid.

A. Emmerling (*Zeits. Anal. Chem.*, 26, 244, Abs. CHEM. NEWS, 57, 15; *J. Anal. Chem.*, 2, 228) describes a new method for the determination of soluble phosphoric acid in superphosphates.

The solution of superphosphates, mixed with calcium chloride, is allowed to flow into a standardised solution of caustic soda, to which some phenolphthalein has been added. The following solutions are required :—

(1) Sodium hydrate, of which 1 c.c. represents about 0·005 P_2O_5.

(2) Calcium chloride solution, made by dissolving 200 grms. $CaCl_2$ in one litre of water.

(3) Penolphthalein, 1 grm. in 500 c.c. of alcohol.

(4) Methyl orange in aqueous solution.

The execution of an analysis is carried on as follows :—

Two hundred c.c. of the solution of the sample prepared in the ordinary manner are well mixed with 50 c.c. solution of calcium chloride. One burette is filled with this mixed solution and a second with the soda solution. Of this latter 20, 10, or 5 c.c. (according to the strength of the superphosphate) are measured into a beaker; 2 c.c. of the phenolphthalein solution are added, and some water, and the superphosphate solution is then run rather rapidly. As soon as the colour begins to grow faint the superphosphate liquor is added more gradually, and at last drop by drop, until the redness has entirely disappeared.

The author next measures off again the same number of the c.c. of the mixed solution of superphosphate and calcium chloride as used above, dilutes with a little water, and mixes with 4 to 6 drops of the methyl orange solution. The liquid is titrated cautiously with the soda solution, finally drop by drop until the reddish colour changes to a yellow or orange yellow.

The smaller number of c.c. of soda solution, as consumed in the titration with methyl-orange, is deducted, from the number obtained in titrating with phenolphthalein. If we have dissolved 20 grms. superphosphate in 1000 c.c. of water, and make up 200 to 250 c.c. by the addition of 50 c.c. of the calcium chloride solution, and if a is the measured quantity of soda, b the solution of superphosphate and calcium chloride consumed, c the soda used for neutralising the free acid, and t the standard of the soda expressed as P_2O_5, the percentage of soluble phosphoric acid in the sample is equal to

$$a - c \times t \times \frac{250 \times 1000 \times 100}{200 \times 6{\cdot}20}$$

This method is applicable to ferriginous superphosphates.

J. Ruffle (*J. Soc. Chem. Ind*, 6, 327—333; Abs. *J. Chem. Soc.*, 1888, p. 87; *J. Anal. Chem.*, 1, p. 455) has contributed an interesting paper on moisture and free acids in superphosphate. The loss of moisture, dried to constant weight, at various temperatures varied in one sample from 12·92 per cent at 38° to 50° C., to 17·93 per cent at 150° C. Drying at the same temperature, 100° C., for different periods, showed a variation of from 9·97 per cent for thirty minutes, to 17·15 per cent for seven hours. The fertiliser dried in its natural state, at 100° C., showed a much greater loss of moisture than when previously rubbed to a fine paste in a mortar.

It is also shown that the soluble phosphoric acid existing in superphosphates is not entirely present as mono-calcium phosphate, and that the exposure of 100° C. drives off more than the true moisture, that is, the adhering uncombined water. It is recommended to determine the moisture in the following manner:—Weigh out 2 to 5 grms. of the phosphate in its natural state on a double watch-glass, place under an air-pump over dry calcium chloride, exhaust, then leave for eighteen to twenty-four hours and weigh.

John Clark (*J. Soc. Chem. Ind.*, vii., 311—312) describes a modification of Perrot's (*Compt. Rend.*, xciii., 495) for the estimation of phosphoric acid as phosphate of silver.

The objections to Perrot's process, when applied to manures and natural phosphates, are—

1. The chlorides which may be present will be estimated as phosphates.

2. The method of separating the phosphates of iron and alumina from the phosphates of lime and magnesia is inaccurate, as it is practically impossible to dissolve out the whole of the phosphate of lime in the manner indicated.

The modifications which the author recommends are—

1. The solution of the phosphate of silver precipitate in nitric acid, and the titration of the silver with sulphocyanide.

2. The neutralisation of the acid solution with caustic soda instead of ammonia to avoid the presence of an excessive quantity of ammoniacal salt, which affects the results.

3. The previous precipitation of the iron and alumina as phosphate with acetate of soda containing free acetic acid.

The following is an outline of the process :—The phosphate is dissolved either in water, nitric acid, or sulphuric acid, the greater portion of the free acid neutralised with caustic soda, and to the cold solution acetate of soda containing free acetic acid is added in excess. If the addition of the acetate of soda produces a precipitate, this must be filtered off, re-dissolved, and re-precipitated with acetate of soda, as before. The filtrate and washings are added to the previous filtrate, then excess of nitrate of silver, which will give an immediate precipitate of phosphate of silver, Ag_3PO_4, and the free acetic acid is neutralised with caustic soda till there is only a faint acid reaction to litmus-paper.

The slightest excess of caustic soda will cause a brown precipitate of oxide of silver, but this oxide of silver dissolves easily on the addition of a few drops of dilute acetic acid.

The precipitate of phosphate of silver, which will contain any chloride which may have been present, is thrown on a filter, thoroughly washed with water, then dissolved off the filter with hot dilute nitric acid, mixed with a little ferric sulphate, and the silver titrated with sulphocyanide, as described by Volhard, and calculated to phosphoric acid.

The precipitate of phosphate of iron and alumina is dried, ignited, and weighed, then dissolved in acid, the iron determined volumetrically, calculated to phosphate of iron, and the balance assumed to be phosphate of alumina; or the oxide of iron may be separated with caustic soda and the alumina in the filtrate weighed as phosphate of alumina, using the precautions recommended by Thomson (*J. Soc. Chem. Ind.*, vol. v.).

Comparative tests on a variety of materials show a close agreement with the molybdic method.

Dircks and Werenskiold (*Landw. Versuchs. Stat.*, 1887, 425—453; Abs. *J. Chem. Soc.*, 1888, 628) have tested the various processes employed for the estimation and separation of tri-calcium from mono- and di-calcium phosphate, namely, the various modifications of the ammonium citrate method. They find that although none

of the methods give a really satisfactory and exact result, Petermann's process is perhaps the most trustworthy.

C. Schindler (*Zeit. Anal. Chem.*, xxvii., 142—146; *J. Chem. Soc.*, 1888, 753; *J. Soc. Chem. Ind.*, vii., 455) describes a volumetric method for the determination of phosphoric acid, based upon the formation of a compound of phospho-molybdate of ammonia of definite composition.

The following solutions are requisite:—

1. *Molybdic Solution.*—To a litre of molybdic acid solution, prepared in the usual manner, 30 c.c. of a solution of citric acid containing 500 grms. to the litre are added.

2. Concentrated ammonium nitrate solution containing 750 grms. to the litre.

3. Dilute ammonium nitrate solution containing 100 grms. to the litre and 10 c.c. nitric acid.

4. Magnesia mixture prepared in the usual manner.

5. Lead solution, 1 c.c. of which corresponds to 0·04 grms. P_2O_5. This is obtained by dissolving 55 grms. lead acetate in one litre of water and a little acetic acid.

6. Molybdate of ammonium solution, 1 c.c. of which corresponds to 1 c.c. lead solution; 25 grms. ammonium molybdate are dissolved in one litre and standardised against the lead solution.

7. Tannin solution; 1 grm. tannin is dissolved in 20 to 30 c.c. of water.

The analysis is conducted as follows:—50 c.c. of the nitric acid solution of the phosphate (0·5 grm. of substance) is mixed with so much of the concentrated solution of ammonium nitrate that after the addition of the molybdic acid solution the mixture shall contain 25 grms. ammonium nitrate per 100 c.c. Then, for each 0·1 grm. of P_2O_5, 100 c.c. of the molybdic acid solution is added, and the mixture heated in a water-bath to about 58° C. The precipitate is allowed to settle for ten minutes, and the liquid decanted and passed through a filter. The precipitate is washed with 50 c.c. dilute ammonium nitrate solution by decantation, and dissolved in 3 per cent ammonia solution. The solution, together with that dissolved off the filter, is brought into a quarter-litre flask, 10 to 20 c.c. magnesia mixture added; after shaking it is made up to 250 c.c. and filtered. 50 c.c. of the filtrate are taken, acidified with acetic acid, and the liquid made up with boiling water to 300 c.c. Lead solution is now added from a burette until a small excess of lead goes into solution, and is titrated back with ammonium molybdate solution, using the tannin solution as an indicator. A drop of tannin solution gives a red colouration with ammonium molybdate, which is visible in a solution of 1 in 400,000, whereas lead molybdate gives no colouration, and lead acetate only a greenish colouration.

Comparative determinations on a variety of materials show a close agreement with the magnesia method.

At a meeting of the directors of the Belgian experiment stations, the following method for the estimation of the phosporic acid soluble in water and in citrate of ammonia was adopted:—

Two grms. of ordinary superphosphate (or 1 grm. of a rich simple, say over 20 per cent) are triturated in a mortar with water and thrown upon a filter. The filter is washed with water until about 200 c.c. have passed through; to the filtrate is added 1 c.c. of nitric acid, and the volume of the solution is made up to 250 c.c. The filter, and the insoluble matter contained in it, is now introduced into a 250 c.c. flask with 50 c.c. of Petermann's alkaline citrate of ammonia solution, and allowed to digest for one hour on the water-bath at a temperature of 38° to 48° C. After rapidly cooling the flask is filled up the mark with water. Of the above filtered liquid (the citrate of ammonia solution), take 50 c.c. and mix it with 50 c.c. of the aqueous solution, acidify with nitric acid, and precipitate with molybdic acid solution. The remainder of the operations remain as for the ordinary estimation of phosphoric acid.

Petermann's alkaline citrate of ammonia is prepared by dissolving 500 grms. of citric acid crystals in water and mixing with 700 c.c. of ammonia of 0·920 specific gravity. Bring the concentration of the liquid to 1·09 specific gravity at 15° C., and add to each litre 50 c.c. ammonia of 0·920 specific gravity.

The report being open for discussion, the President called attention to the dependence of amount of soluble phosphoric acid on the size of filters used during its extraction, and thought it would be well for the committee to recommend a definite size of nine centimetres.

Professor Frear spoke of differences due to variations in moisture in different laboratories.

Mr. Gascoyne said the variations in moisture was not proportional to the variations in phosphoric acid, and that such differences as 12 and 19 per cent could not be due to anything but carlessness, the highest determinations of moisture being accompanied by highest percentages of phosphoric acid.

Professor Lupton, on examining the results, said he could see no way to harmonise variations.

The President thought the publication of these results would be most beneficial to the Association, and that results another year would be sent in with greater care.

The President then introduced the subject of the use of pumps for extracting soluble phosphoric acid, considering it an advantage where much work was to be done.

Mr. Gascoyne spoke of quick work with molybdate and magnesia solutions, allowing them to stand but five to ten minutes for the yellow precipitate, and not more than fifteen for magnesia precipitate.

Mr. Gaines's and Mr. Richardson's experiences confirmed his observations.

(To be continued).

NOTICES OF BOOKS.

A Text-Book of Elementary Metallurgy for the Use of Students. By Arthur H. Hiorns, Principal, School of Metallurgy, Birmingham, and Midland Institute. London: Macmillan and Co.

This little work is strongly "examinational," the author being probably of opinion that the system will "last his time." To 172 pages of the actual text, the instructive portion of the book, there are superadded not fewer than 64 pages of examination questions set by the Science and Art Department during the last twenty years. This section of the work is doubtless intended for the convenience of students, or rather of young men preparing for examination, and of "coaches." But the list makes no mention of the time when the various questions were set, nor of the periods of their recurrence, and thus it does not show either the "coach" or his pupil what subjects must be especially "got up," or what may be safely overlooked.

Among these questions we notice one which is decidedly unfair, namely, "What is a metal?" Here eminent chemists differ widely among themselves, not only, *e.g.*, arsenic and silicon, but even tin, being by some authorities held to be metals, and by others to be non-metallic elements. Here, therefore, the student may easily commit himself, except he knows the peculiar views of the examiner. Another question is, "What is meant by the term 'autogenous soldering?'" We have always known this term to be applied to the Richemont process where two sheets of lead are united at their edges by letting one overlap the other, and then running, by means of a flexible tube, the flame of an oxy-hydrogen blowpipe along the junction, as it is always done in fitting up the lead chambers at sulphuric acid works. Professor Hiorn, however, tells us that "sheets of lead and tin can be rolled into one compact sheet called autogenous soldering." We submit that if *two* metals are present the process is not

autogenous, and that the presence of tin would be fatal in the lead chambers. Now, if Prof. Hiorn's definition of autogenous soldering is not the one recognised at South Kensington, woe be to his students.

The body of the work has few blemishes. But, in our opinion, the examination-questions had better have been omitted, and their place occupied by more useful matter. A more copious index would have been an improvement.

The Blowpipe in Chemistry, Mineralogy, and Geology; containing all Methods of Anhydrous Analysis, many Working Examples, and Instructions for Making Apparatus. By Lieut.-Colonel W. A. Ross, R.A., F.G.S., &c. Second Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

The fact that a second edition of this book has been found necessary proves that an increasing interest must be felt in blowpipe analysis. This fact may serve as a set-off to the circumstance, mentioned in a foot-note, that "the City and Guilds of London Institute have, quite recently, by the advice of an irresponsible chemist, cut out blowpipe analysis from their curriculum. It is still untaught at the Royal School of *Mines!*" If there is here no mistake, this is a fact much to be regretted. It is to be hoped that in these days of "technical education" such a state of things cannot long be suffered to continue.

The author differs from many authorities in considering that the use of blowers, worked by foot or hand, is not merely permissible, but in some cases preferable to the mouth-blower, as affording, if duly proportioned to the bulk of the flame, a "greater and a more localised heat." He takes an independent standing also in recommending a gas-flame as the source of heat, always excepting cases where the operator is testing for sulphur and its compounds.

He recommends his students to use a "hot-gas lamp," worked by a foot-blower, whenever procurable. We do not at all question the dictum of Col. Ross when saying that he has worked twelve years with oil-lamps and twelve years with gas, and has found no *great* difference in the results. Still we can scarcely see that the use of gas can be indifferent in all the cases where sulphur reacts strongly upon the substances under examination.

The aluminium plate as a support, first devised by Col. Ross, has approved itself in practice, and now seems to have been generally adopted, except at Freiberg, and at the "J. C. Green School of Science" in New Jersey.

A very commendable feature in the work, or we may rather say in the author's system, is the endeavour to dispense with costly and cumbersome articles of apparatus wherever possible. In this undertaking he has been very successful.

The additional matter first appearing in the edition consists of exercises in the determination of minerals by the blowpipe alone, with the solutions by a correspondent of the paper in which they were first published.

That Col. Ross has done good service in promoting, improving, and facilitating blowpipe analysis is beyond all question.

The Introductory Address to the Eighth Lecture Course at the Albany College of Pharmacy. Delivered October 1st, 1888. By Willis G. Tucker, M.D., Ph.D., Professor of Chemistry. Published by the Class, Albany, N.Y.

Sound, earnest advice, not specially applicable to pharmacists, but deserving to be marked, learned, and inwardly digested by students in every science! Nay much of what we here find may be taken to heart by numbers who are never seeking to become *savants*. The speaker insists, first and foremost, upon exactitude. He suggests that young men should make a thorough study of some one of the natural sciences, and acquire in the laboratory or museum "the habit of exact observation and precise measurement and statement, in such way that it will stick to them for life."

The reader is next reminded that science is painstaking, laborious, patient. He is referred to the lives of Agassiz and Darwin to learn what diligence is.

The scientific worker, further, is governed by a judicial spirit. Here we find reference to certain "paper philosophers" who criticise theories which they are unable to comprehend. It is admitted with regret "that clever partisans with their specious and fallacious reasonings, their rhetorical vapourings and heated arguments, carry the multitude along with them."

True scientific work also is not inspired by a love of gain. In developing this part of his theme Dr. Tucker might have added that the highest results in every science are necessarily unremunerative. He speaks of a "class of middlemen, a kind of rear-guard science, ever on the alert to seize upon those ideas which can be turned to practical account, and this class secures the profit and often much of the credit of discovery." We do not know whether this class, instead of being called a rear-guard, might not better be designated as camp-followers eager to plunder the wounded.

Perhaps the lessons here enforced are not novel. But until they are apprehended by the public at large, they cannot be too often or too emphatically reiterated. Dr. Tucker, therefore, has spoken well and wisely.

CORRESPONDENCE.

THE USE OF PEROXIDE OF HYDROGEN FOR THE DETERMINATION OF THE METALS OF THE IRON GROUP.

To the Editor of the Chemical News.

Sir,—I see from the paper under the above heading copied from the *Comptes Rendus*, vol. cvii., p. 997, into the Chemical News (vol. lix., p. 15), that its author, M. Adolph Carnot, recommends the volumetric estimation of manganese by means of hydrogen peroxide and ammonia, the solution of the manganous salt to be precipitated by these reagents, excess of the oxidant expelled by boiling, and the manganic hydroxide to be treated by any well-known procedure.

If M. Carnot quantitatively examines his method he will find that manganic hydroxide obtained as he proposes approximates in composition to Mn_7O_{13}, and varies in composition, so that as a basis for the volumetric estimation of manganese, the results may differ six per cent.—I am, &c.,

Norman McCulloch.

Laboratory of Clyde Iron Works,
(by Tollcross), Glasgow,
January 14, 1889.

ELECTRIC SUGAR.

To the Editor of the Chemical News.

Sir,—The questions put by Mr. G. A. Keyworth, in the last number of the Chemical News (vol. lix., p. 24), as to "electric sugar," have been, to a great extent, already answered in an article written by ourselves, and which appeared in the November number of the new journal *Sugar*. Referring to a trial of the so-called "electric process," we then stated that "from examination of the sugar produced in this experiment, it is evident that it had, at one period of its existence, assumed the form of loaf sugar, or cubes, and from this state, possibly by means of the granulators alluded to in the report, after

being damped, it had been reduced to small pieces, which were subsequently separated by sieves of various sizes, thereby forming samples of comparatively even grade. This explanation of the *modus operandi* is corroborated by the fact that pieces of hard sugar, of considerable size, passed out of the apparatus during the progress of the trial, owing doubtless to the unfortunate break-down which is said to have taken place. As a matter of fact, granulated sugars of an exactly similar appearance may be readily obtained by breaking up loaf sugar, or cubes, and sifting the rough powder through a set of sieves so as to separate the sugar into various grades."

We may add that the so-called "electric sugar" is no purer than the usual run of loaf sugar and cubes which contain only a very minute amount of impurity. The trace of glucose present in some samples of "electric sugar" is due to the sugar having been kept for some time in a moist state previous to being manipulated in the way already described.—We are, &c.,

NEWLANDS BROS.

Laboratory, 27, Mincing Lane, E.C.,
January 15, 1889.

SCIENCE AND ART DEPARTMENT.

To the Editor of the Chemical News.

SIR,—With regard to the strictures of Mr. Bloxam on my answer to "Student," I may say that I did not think it necessary to inform a student of organic chemistry how to prepare a solution containing inorganic bases for the detection of organic acids. I certainly did not mean "separation of the inorganic bases as usual" to imply what Mr. Bloxam understands by it, viz., removal of the metals, group by group, by the ordinary methods of inorganic analysis, but rather treatment, as Mr. Bloxam says, with Na_2CO_3, and further—which Mr. Bloxam does not say—treatment with H_2S in the presence of such metals as As, Sn, or Sb soluble in alkaline solutions. I may also remark that I doubt whether "Student" will be able to detect the organic acids mentioned decisively, when *mixtures* of them or their salts are heated with dilute or concentrated H_2SO_4.—I am, &c.,

W. E. YOULE.

25, Deptford Lower Road,
January 14, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Bulletin de la Société Chimique de Paris.
Vol. l., No. 11.

Rapid Method for the Analysis of Industrial Waters, with a View to their Chemical Purification.—Leo Vignon.—The author's method comprises two distinct operations. He first determines by saturation with a standard solution of calcium hydroxide the carbonic acid other than that existing in natural carbonates, using phenolphthalein as indicator. He then measures, by means of a standard solution of sodium carbonate, the proportion of that salt necessary to precipitate as carbonates all the soluble salts of calcium and magnesium, using the same indicator. In both cases the phenolphthalein does not take and retain its characteristic rose colour until the lime or the sodium carbonate is in excess in the liquid.

Action of Hypophosphorous Acid upon Benzoic Aldehyd; Formation of Dioxyphosphinic Acid.—J. Ville.—Hypophosphorous acid is capable of combining with benzoic aldehyd, so as to yield a triatomic monobasic acid, the dioxyphosphinic acid, which might otherwise be called dioxybenzylphosphinic acid.

On "Adjacent" Metaxylidine and its Identity with the Orthoxylidine of Wroblewsky.—E. Noelting and B. Pick.—The metaxylidine in question is distinguished from all its isomers by the great solubility of its sulphate, by its resistance to acetylisation, its high fusion-point, and the great stability of its acetylic derivative. It is present in small quantity only in commercial xylidine, so that a large quantity of material must be taken for its isolation.

On the Azoxylenes, the Diamido-dixylenes, and the Colouring-matters derived from the latter.—E. Noelting and B. Strecker.—The authors give a table of the shades obtained by diazotising all the bases which they have obtained, and conjugating them with naphthionic acid, α-naphthol-α-sulphonic acid, and naphthol-disulphonic acid, R.

On the Sulphonic Acid of the Methylic Ether of Phenyl-carbaminic Acid.—E. Noelting.—The amido-sulphobenzoic acid of Hentschel should apparently be considered as a phenylcarbamine-sulphonic acid, and the direct introduction of carboxyl into aniline by means of chlorocarbonic ether becomes in general very problematic.

On a New Franceine derived from Tetrachlorised Benzene.—MM. Georgesco and Mincou.—This franceine, $C_{16}H_4O_6Cl_3$, differs absolutely from that obtained from the chloro-derivative. In fragments it is of a greenish black colour, with a metallic lustre and a conchoidal fracture. When finely-powdered it is black. It is very soluble in alkalies. The neutral potash or soda solution has a blackish red colour. In this state it may serve as an ink or for painting in water-colours. In this state it gives an earthy-red colour. It is but sparingly soluble in alcohol; the yellowish red colouration is not dichroic, nor is the rose-coloured solution in glycerin.

The Determination of Sugar by Fehling's Liquor.—H. Causse.—This determination is interfered with by the precipitation of cuprous oxide, which, towards the end of the process, occasions bumping, so that it is necessary to operate at a point below ebullition. The author avoids this difficulty by adding to the cupro-potassic liquid a solution of potassium ferrocyanide.

On Anagyrine.—E. Hardy and N. Gallon.—Anagyrine, $C_{14}H_{18}N_2O_2$, is the essential principle of *Anagyris fœtida*, a leguminous plant growing around the basin of the Mediterranean.

Transformation of Methyl-valeryl-acetylene into Hexyl-acetylene.—A. Béhal.—Sodium, by mere action of presence, converts a substituted acetylenic carbide into a true acetylenic carbide.

Action of Phosphorus Perchloride upon Malonic Acid.—A. Béhal and V. Auger.—The authors obtain by this reaction a mixture of phosphorus oxychloride and of malonyl chloride.

Action of Phosphorus Perchloride upon Acetophenone.—A. Béhal.—This paper is not adapted for useful abstraction.

Homopterocarpine and Pterocarpine from Santal Wood.—P. Cazeneuve and L. Hugounenq.—Homopterocarpine is probably a kind of methylated polyorcine, comparable to the polyglucosides. Pterocarpine is probably an inferior homologue containing the same fundamental nucleus, and differing only in its substitution radicles.

On Manganese Oxalate.—J. Castelhaz.—Oils prepared with manganese oxalate may be advantageously substituted for drying oils in all their applications by reason of beauty and other properties. From 2 to 5 per cent of manganese is sufficient for boiling oils. The manganese salt is first ground up with 1 or 2 parts of the

oil to be boiled, and this mixture is added very gradually to the bulk of the oil, stirring well. The oil is heated very gradually at first, but after the escape of the gases it may be boiled in the ordinary manner.

No. 12, December 20, 1888.

The Presence of Benzene Vapour in Lighting-Gas and its Determination.—M. Berthelot.—In 1876 the author found that the gas of Paris owes much of its illuminating power to the vapour of benzene. He estimated its proportion by weighing the crude nitrobenzene, obtained by passing the gas through fuming nitric acid.

Preparation of Concentrated Formic Acid.— M. Maquenne.—By two successive distillations over sulphuric acid, the ordinary acid of commerce is easily converted into a product containing 98 per cent of real acid. The crude yield is about 55 per cent.

Researches on Rhodium.—E. Leidie.—The author first examines former processes employed for preparing rhodium sesquichloride; he describes his method for preparing the anhydrous sesquichloride, the corresponding hydrate; the double chlorides of rhodium and potassium, rhodium and sodium, and rhodium and ammonium. He then describes rhodium sesquioxide, sesquisulphide; the neutral and basic rhodium sulphates and the double oxalates. The author considers that although rhodium is distinguished from such metals as aluminium, iron, and chromium, by its inability—as far as we can judge at present—of forming alums, it approaches them, nevertheless, by certain common characters, such as the formation of a sesquichloride and double chlorides, a sesquioxide with a series of salts, a sesquisulphide and double sulphides, a regular series of double oxalates, and lastly a chloramidide and its derivatives which approximate it, especially to chrome. We may therefore consider it as the analogue of chrome among those metals known as the platinum group.

Conditions of the Formation of Durol and Production of Mono-benzyl-durol by the Aluminium Chloride Method.— M. Beaurepaire.—The author obtains this compound by heating together in a very dry flask, fitted with a reflux cohobator, 10 parts purified durol, 7 parts dry benzyl chloride, 50 dry carbon disulphide, with traces of aluminium chloride.

MISCELLANEOUS.

The Sanitary Institute.—At a meeting of the Council of this Institute, held 9th January, G. J. Symons, F.R.S., in the chair, it was decided to hold two courses of twelve lectures for Sanitary Officers, the first course to commence in March and the second in October. 64 Members and Associates were added to the Register, and 20 applications read for election at the next meeting.

City and Guilds of London Institute.—Technical College, Finsbury.—A course of six Evening Lectures on the "Science of Brewing" will be delivered by Dr. E. R. Moritz, F.I.C., F.C.S., commencing January 23rd.

Central Institution, Exhibition Road.—During the Spring Term, Professor Armstrong will give about ten lectures on "Some of the More Important Current Problems in Chemistry" on Mondays at 4.30 p.m., commencing Monday, January 21st. The following subjects will be dealt with as far as time permits:—The nature of chemical change; the interdependence of chemical change and electrolysis; the molecular composition of gases, liquids, and solids; the nature of solutions; physical constants; laws of substitution and isomeric change as bearing on the problem of the nature of chemical change; valency; geometrical isomerism and allo-isomerism.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose o giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Arborescent Crystals.—Will any of your readers kindly inform me if any arborescent forms of crystals have been observed other than the so-called lead and zinc tins? I have made some with salts of copper, cobalt, &c., and before communicating my results I should like to know if they are original.—H. O. H.

MEETINGS FOR THE WEEK

MONDAY, 21st.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. Lecture I.
TUESDAY, 22nd.—Institute of Civil Engineers, 8.
—— Society of Arts, 8. "Some Recent Movements in relation to the Applied Arts," by Sir James D. Linton, P.R.I.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 23rd.—Society of Arts, 8. "Electric Meters for Central Stations," by Prof. George Forbes, F.R.S.E.
—— Geological, 8.
THURSDAY, 24th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
FRIDAY, 25th.—Quekett Club.
—— Society of Arts, 8. "The Asiatic Colonization of East Africa," by H. H. Johnston, F.R.G.S.
—— Royal Institution, 9. "Meteorites and the History of Stellar Systems," by Prof. G. H. Darwin, F.R.S.
SATURDAY, 26th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.
—— Physical, 3. "Notes on Polarised Light; on the Structure of Natural Diffraction Gratings of Quartz; on Ahrens's Modification of Delezenne's Polariser; and on the Use of Two Quarter-wave Plates in combination with a Stationary Polariser," and "Note on a Relation between Magnetisation and Speed in the Dynamo Machine," by Prof. S. P. Thompson, D.Sc. "On the Divergence of Electro-motive Forces from Thermo-chemical Data," by Prof. E. F Herroun.

One Shilling, Post Free.

THE TRUE POSITION OF PATENTEES. By HENRY MOY THOMAS. Explaining the regulations now in force in all the principal countries and the combined effects of Home, Foreign, and Colonial Patent Laws.

AYRTON and THOMAS, 59 and 60, Chancery Lane.

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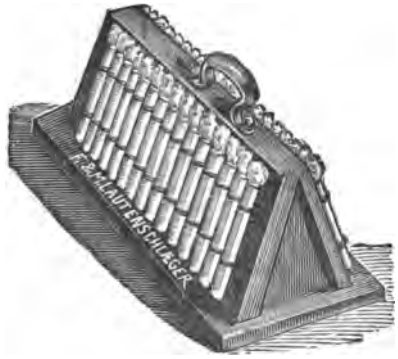

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THE CHEMICAL NEWS.

Vol. LIX. No. 1522.

DECOMPOSITION OF NICKEL AND COBALT.

Though we have not yet obtained the original paper laid before the Chemical Society of Munich by Dr. Krüss, we lay before our readers such further particulars as have come under our notice. It does not now appear, as we had supposed from the first announcement of the discovery, that cobalt and nickel have been entirely split up into three hitherto unknown compounds, one common to both the metals whilst each of the other two was found only in one of them. On the contrary, as we understand the most recent intelligence, Dr. Krüss has found in each of these metals an unknown substance to the extent of 2—3 per cent. After this new body is eliminated, cobalt or nickel—as the case may be—still remains, though with modified properties. The salts of pure cobalt, or new cobalt, are said to be of a violet colour, and those of pure nickel of a dark green. Dr. Krüss was occupied with re-determining the atomic weights of cobalt and nickel; to this end he treated carefully weighed portions of cobalt or of nickel with a neutral solution of gold chloride, and weighed the gold which was eliminated. The results of these operations were not constant, and after various other attempts to detect any possible source of error the gold deposited was closely examined. It was found that after having been dissolved in nitro-hydrochloric acid and reduced with sulphur dioxide there was a loss of weight, and that the washing-waters had a green colour. On concentration these washings gave a colourless liquid, which turned green on the addition of hydrochloric acid, and gave a white deposit on the addition of caustic soda or ammonia, insoluble in the former.

As these reactions could not belong to cobalt or nickel Dr. Krüss sought to procure a larger quantity of the unknown material. He ignited freshly precipitated cobalt or nickel oxide with caustic alkali, extracted the melt with water, and obtained a solution possessing the characters above mentioned, though the pure nickel oxide or cobalt oxide was left undissolved. The solution on treatment with ammonia gave a bulky precipitate of hydroxide. On ignition this yielded a white oxide, giving a brown malleable metallic powder by reduction with charcoal. From the solution ammonium sulphide threw down a deep brown sulphide, soluble in acids. From these reactions the presence of a new metal was inferred. Dr. Krüss is engaged with a further investigation of this substance as well as with a re-determination of the atomic weights of nickel and cobalt.

We lay before our readers the following portion of a letter which has been kindly forwarded us by Professor Krüss:—

"I have in fact succeeded in splitting up nickel and cobalt each into two parts, and both these metals have one component in common. In concert with my colleague, I sent a brief notice on this subject to the *Berichte*, which will appear in Berlin on Monday next (21st inst.). The matter communicated in this short memoir has been intentionally kept very scanty, and I gave as little room as possible to speculation for fear of being led to assertions which I might perhaps soon have to withdraw. Meantime, I have fully confirmed our first observations, and we have now about ten different methods by which we can resolve these bodies, hitherto regarded as elementary, each into two parts. We shall soon give a full report on our results, but in the meantime I may inform you, as a curious fact, that we have succeeded in obtaining *green* so-called nickel salts from *red* cobalt salts and the *colourless* salts of the substance which accompanies both metals, and further, in transforming some green nickel salts into red cobalt salts and other components. This may perhaps sound alchemical, but it cannot be denied. As for the spectra of the three components of cobalt and nickel, we have not yet, with the ordinary experimental arrangements, observed any characteristic lines. This is doubtless the reason why hitherto no spectral lines have been found common to pure cobalt and nickel.

VICTOR MEYER'S VAPOUR DENSITY METHOD MODIFIED FOR USE UNDER DIMINISHED PRESSURE.

By THEO. W. RICHARDS.

The many researches which have recently been published upon the vapour densities of substances which are easily decomposed, suggested to the writer the great desirability of some good method of determination which could be used under reduced pressure. The only methods as yet used for this purpose are: first, the method of Hofmann, which is open to the great objection of the necessity of measuring the vapour over mercury, which makes it impossible to use a temperature much above 200° C.; and second, the application of Dumas's method, used by Friedel and Crafts* for the determination of the density of iron chloride, which is open to all the objections to Dumas's method, and is at the same time complicated in execution.

For the application of Victor Meyer's method to reduced pressures, it is only necessary that we have in the whole interior of our apparatus an artificial atmosphere, of constant low tension, which not only pervades the vapour density bulb itself, but also is in connection with both surfaces of the water over which the displaced air is collected.

The apparatus used may be divided into three parts: first, the vapour density bulb itself, which is exactly like that described by Grünwald and V. Meyer†; second, the apparatus for receiving the displaced air; and third, the arrangement to secure a constant reduced pressure.

The apparatus for receiving the replaced air is an upright U-tube, having an internal diameter of about 1·3 c.m. and a height of 50 c.m., the end of each arm being drawn out to allow of rubber connections. A small tube is melted into each side near the bend, and through one of these the displaced air from the Meyer apparatus enters and replaces the water, which rises in the other arm, and may be drawn out or let in through the other side tube by means of an arrangement of tubes, nipper taps, and a flask, to preserve constant level.

As before said, in one arm of the U-tube the air is collected as it comes from the Meyer apparatus, and from this arm it is driven out at the top after the vapourisation is ended, and measured in an ordinary eudiometer at the atmospheric pressure and temperature. The other arm of the U-tube is connected with the constant pressure arrangement, which must now be described.

In seeking after material for such an apparatus mercury was of course first decided upon, and an arrangement somewhat like Mariotte's flask was set up, but it was found that with heavy mercury columns it was impossible to secure constant pressure. If was evident that if mercury was to be used it must be in a small column. Accordingly, the following apparatus, consisting of two parts, was arranged:—

The tube leading from the U-tube is led through the stopper of a wide barometer tube, 17 m.m. in diameter, which we may call the regulator, and ends at a height of 520 m.m. above the free surface of mercury, in which the

* *Comptes Rendus*, cvii., 301.

† *Berichte d. Deutsch. Chem. Ges.*, xxi. (1888), 688.

lower end of the latter is immersed. Another tube, just penetrating this same stopper, is led to the depth of 200 m.m. in mercury contained in a closed vessel, which is connected with the water-pump. Let us now suppose that the pump is set in motion, and that the barometer stands at 740 m.m., the available pressure of the pump being then about 730 m.m. Mercury of course then rises in the regulator to the height of 730 − 200 m.m. = 530 m.m., or 10 m.m. above the end of the tube connected with the first part of the apparatus. It is evident that this extra 10 m.m. *can have no effect on the tension of the air in the U-tube* and Meyer bulb; this tension is influenced only by the distance between the end of the tube and the free surface of the mercury in the dish below. As this distance is constant the tension must be constant, no matter how the pump varies in action or what changes there may be in the atmospheric pressure, provided always that the mercury does not fall below the end of the tube above mentioned. Of course any addition of volume in the Meyer bulb merely causes air to quietly bubble up through the small layer of mercury, and a barometer tube interposed between the regulator and the U-tube showed that the compensation was as nearly perfect as could be desired. Of course, by altering the lengths of the tubes and the heights of the mercury columns any desired pressure may be secured; but it is always better to have the column in the regulator stand at a height of about 10 m.m. above the end of the small tube inside.

The exact manner of working the apparatus cannot possibly be explained without an illustration, which is now being made, and which will appear later in a more complete description of the whole apparatus.

Two determinations have already been made by this method, and the results show that the apparatus is thoroughly practical. No difficulty was found in making the joints tight, and the pressure remained completely constant for an indefinite length of time. The time occupied by an experiment is not much longer than that occupied by an ordinary Meyer determination, as the pressure very soon reaches constancy.

The substance used was pure toluol, boiling at 110°; it was weighed out in a small sealed tube, the end of which was broken off just before introduction into the apparatus. The temperature used for vapourisation was 100° C. (steam), and the tension used in each case was 220 m.m.—the difference between the atmospheric pressure and the height of the mercury in the barometer connected with the apparatus. The vapourisation was very rapid and the conclusion of the experiment perfectly definite. Of course, in the calculation allowance was made for the tension of aqueous vapour, and through the whole course of the experiments all possible precautions were taken to procure trustworthy results. Below are the data of the two experiments which have thus far been made:—

I.

Weight of toluol taken	0·0247 grm.
Vol. of air at 738 m.m. and 12° C..	6·8 c.c.
Tension	220 m.m.
Temperature of bath	100°
Result = vapour density of toluol ..	3·06

II.

Weight of toluol taken	0·0338 grm.
Vol. of air at 738 m.m. and 12° C..	9·05 c.c.
Tension	220 m.m.
Temperature of bath	100°
Result = vapour density of toluol ..	3·15

The volume of the air while yet in the apparatus under diminished pressure was about 25 c.c. to 35 c.c. The two results average 3·10, the theoretical density of toluol with reference to air being 3·18. The results, then, are as good as those by Meyer's method at ordinary atmospheric pressure.

It is possible that the same end might be accomplished by a much simpler piece of apparatus, substituting for the two mercury pressure regulators and the pump merely a large glass globe, which has been previously exhausted. If the globe were large enough the very small volume of vapour evolved in the Meyer bulb would have a scarcely perceptible effect on the tension of this confined artificial atmosphere, and any slight error might be easily corrected by careful application of the pump. Experiments with this simplified apparatus will be tried in the near future.

The object of the method was to determine with greater certainty the density of several substances which have recently been investigated in this laboratory; among others, iron and aluminium chlorides; but the method is a very general one, and will prove useful not only for those substances which decompose, but also because it will often do away with the necessity of using high temperature baths and consequent complications.

In conclusion the writer would express his heartiest thanks to his friends Messrs. W. P. Bradley and H. E. L. Horton, whose encouragement, advice, and assistance helped very materially in the carrying out of the idea; and also to Prof. Dr. Geh.-Req.-Rath Victor Meyer for his kindly permitting the use of the excellent advantages of his magnificent new laboratory.

Göttingen, Jan. 12, 1889.

NOTE ON THE DETERMINATION OF THE FREE CAUSTIC ALKALI IN SOAP.

By J. A. WILSON.

Soap, made by the so-called cold process, may contain both the caustic alkali and free oil or fat. When such soaps are dissolved in alcohol, to estimate the free alkali by titration with N/10 acid and phenolphthaleine, the free alkali immediately saponifies the free glycerides in the usual manner. Hence, a soap which by a qualitative test showed free caustic alkali, would not do so after treatment with spirit. The author therefore prefers to estimate the alkali in total by titration with normal acid and methyl orange; and in another portion, the alkali needed to neutralise the fatty acids isolated from the soap. Any silicate, carbonate, or borate in the soap would, of course, vitiate the results; but these can be accurately estimated, if necessary, by other means.

The Laboratory, Tottington Mill,
Jan. 16, 1889.

ACTION OF THE HALOGENS ON RUFIGALLOL DICHLORHEXHYDROXY-ANTHTRAQUINONE.

By C. S. S. WEBSTER and L. G. HUNT.

By the action of chlorine upon rufigallol in acetic acid solution of 60 per cent, it is converted into a substance crystallising in nodules composed of microscopic prisms of a brilliant red colour.

The anhydrous substance on analysis was found to contain 18·96 chlorine and (calculated for $C_{14}Cl_2H_6O_8$) 19·2 per cent chlorine.

That the reaction is one of simple substitution we conclude from its being unattended with any evidence of decomposition, as well as from the properties of the compound in question. The derivative is, therefore, dichlorhexhydroxy-anthraquinone.

By the action of bromine upon rufigallol in acetic acid solution at 80° C. we obtain a derivative crystallising from absolute alcohol in microscopic needles of a light red colour.

We intend shortly to publish an account of these researches in detail.

ON THE

VOLUMETRIC DETERMINATION OF SULPHUR BY MEANS OF BARIC CHLORIDE.

By C. and J. J. BERINGER.

The titration of sulphates by means of baric chloride in the presence of hydrochloric acid has the well-known disadvantage of requiring an excess of baric chloride, leaving, towards the end, a solution which is precipitated equally by baric chloride and sulphuric acid. In addition, the interference of nitric acid and nitrates excludes the use of nitre for the oxidation of the sulphides—and fusion with this reagent is in many cases the quickest and most convenient method of bringing the sulphur into solution.

The effect of nitric and hydrochloric acids on the titration is shown by the following experiments. A standard solution of barium chloride (100 c.c. = 1 grm. of sulphur) was used and tested against a solution of sulphuric acid of equivalent strength. The assay solution had a volume of 500 c.c. in each experiment, and was titrated boiling. The finishing point was determined by withdrawing portions of 5 c.c. and testing after filtration with dilute sulphuric acid. The first indication of a precipitate was taken as the finishing-point.* 20 c.c. of the sulphuric acid were used with varying quantities of the acids, and the results on titrating were :—

	C.c.	C.c.	C.c.	C.c.
Hydrochloric acid present.	0	1	2	5
Baric chloride required ..	20·0	20·0	19·7	12·5
Nitric acid present	0	1	2	5
Baric chloride required ..	20·0	19·5	18·0	10·0

In gravimetric work this interference may be overcome by using an excess of baric chloride, but it is evident that for volumetric work the removal of such a disturbing agent will be an advantage. With this object we tried a series of experiments.

Effect of Acetic and Citric Acids and of Sodium Acetate.—Experiments similar to the last, to compare the effect of these with the other acids, were made, using 20 c.c. of the sulphuric acid under the same conditions as before. The results were :—

Acetic acid present .	0 c.c.	5 c.c.	50 c.c.	100 c.c.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.
Citric acid present	0 grm.	1 grm.	5 grms.	
Baric chloride required..	20·0 c.c.	20·0 c.c.	20·0 c.c.	

These results being sufficiently satisfactory, and acetic acid being more convenient for use, we tried the effect of varying quantities of sodic acetate in the presence of 5 c.c. of acetic acid.

Sodium acetate added	0 grm.	1 grm.	10 grms.	50 grms.
Barium chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c.	20·0 c.c.

It next remained to determine the quantity of baric chloride solution required in 500 c.c. of water, and in the presence of these substances to give an indication when 5 c.c. were withdrawn and tested with sulphuric acid. The results were :—

Conditions of the assay solution.	Baric chloride required.
Water only	0·05 c.c.
With 10 grms. of sodium acetate and 5 c.c. of acetic acid	0·05
The same with 5 grms. of nitre ..	0·10
The same with 5 grms. of sodium chloride	0·10

* The quantity of sulphur thus withdrawn did not in any case amount to 0·5 m.grm

To determine whether the same finishing point would be obtained on testing the filtered portions with baric chloride as is got on testing with sulphuric acid, a titration was made with 20 c.c. of the sulphuric acid, 5 c.c. of acetic acid, and 10 grms. of sodium acetate, and the usual volume of 500 c.c. In testing, two portions of 2 c.c. each were filtered into two test-tubes after each addition of the standard. One series was tested with sulphuric acid and the other with dilute baric chloride. The finishing point in each series was the same. We, however, in finishing, adopt the sulphuric acid test, since it is better to look for the appearance of a precipitate in the test-tube than to watch for its disappearance, except when the quantity of standard solution required is not approximately known, in which case we add barium chloride in testing, so as to get, by the appearance of the precipitate an indication of an approach to the finish.

Effect of Varying Sulphur.—The conditions in these and the following experiments were, except it is otherwise stated, 500 " c.c." bulk with 10 c.c. of acetic acid and 10 grms. of sodic acetate.

	C.c.	C.c.	C.c.	C.c.	C.c.
Sulphuric acid added ..	5	10	20	50	100
Baric chloride required ..	5·0	10·0	20 0	50·0	100·0

Effect of Varying Temperature.—With 5 c.c. of the sulphuric acid titrated at 15° C., 5 c.c. of baric chloride were required; but with larger quantities the results when titrated cold were altogether unsatisfactory.

Effect of Foreign Salts.—In these experiments 20 c.c. of the sulphuric acid were used with varying amonnts of the salt whose effect we desired to determine. The other conditions of the titration were as before.

Sodic chloride added ..	0 grm.	5 grms.	10 grms.
Baric chloride required..	20·0 c.c.	20·0 c.c.	19·7 c.c.
Ammonic chloride added	0 grm.	5 grms.	10 grms.
Baric chloride required..	20·0 c.c.	20·0 c.c.	19·5 c.c.
Calcic chloride added	0 grm.	1 grm.	2 grms. 5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	19·2 c.c. 19·0 c.c.
Zinc chloride added	0 grm.	1 grm.	3 grms. 5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20 0 c.c. 20·0 c.c.
Ferrous chloride add.	0 grm.	1 grm.	3 grms. 5 grms.
Baric chloride reqrd.	20·0 c.c.	19·7 c.c.	19·5 c.c. 19·0 c.c.
Ferric chloride added	0 grm.	1 grm.	3 grms. 5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c. 20·0 c.c.
Copper chloride add.	0 grm.	1 grm.	3 grms. 5 grms.
Baric chloride reqrd.	20·0 c.c.	20·0 c.c.	20·0 c.c. 20·0 c.c.
Potassic nitrate add.	0 grm.	1 grm.	5 grms. 10 grms.
Baric chloride reqrd.	20·0 c.c.	20.0 c.c.	20·0 c.c. 19·0 c.c.
Potassic nitrite added ..	0 grm.	1 grm.	5 grms.
Baric chloride required ..	20·0 c.c.	20·0 c.c.	20·0 c.c.
Sodic phosphate added		0 grm.	1 grm.
Baric chloride required		20·0 c.c.	22·5 c.c.
Sodic arsenate added		0 grm.	1 grm.
Baric chloride required		20·0 c.c.	20·5 c.c.

Phosphates and arsenates interfere counting as sulphur, but can be thrown out by the addition of ferric chloride to the assay solution before boiling. The ferric precipitate need not be removed before titration; its presence will be an advantage rather than otherwise, as it helps to give a clearer filtrate for testing.

The non-interference of as much as 5 grms. of nitre allows of the use of this reagent for oxidising the ore by fusion.

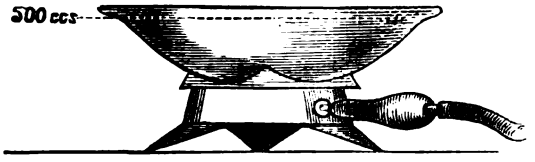
Mode of Working.—Those substances, such as pyrites, the sulphur of which can be got into solution as sulphate by treatment with nitric acid without any separation of globules of sulphur, are treated with this acid, evaporated, taken up with hydrochloric acid, and again evaporated to a small bulk, diluted with water, and transferred to a large

evaporating dish. Ten grms. of sodic acetate and 5 c.c. of acetic acid are then added, and the solution diluted to half a litre and boiled.

With grey copper and similar substances which are not easily oxidised with nitric acid, 1 grm. of the substance is ground in a small mortar with 5 grms. of nitre and transposed to a porcelain or platinum dish. The mixture is fused for a quarter of an hour at a low temperature over a bunsen, and when cold placed in the large evaporating dish. Extract with hot water, add sodic acetate and acetic acid, and dilute to half a litre. The dish used for fusion should be removed, but there is no necessity for filtering.

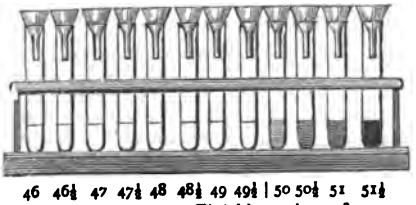
With insoluble sulphates such as barytes, 1 or 2 grms. of the substance is fused with 5 grms. of fusion mixture, the melt extracted with water, filtered into the dish, acidulated with acetic acid, and diluted to half a litre.

The solution before titration must contain no free mineral acid, but 5 or 10 c.c. of acetic acid should be present. It must contain 10 grms. of sodium acetate or sufficient to convert any free mineral acid into its corresponding sodic salt, and if chlorides, nitrates, or sulphates of the metals are present, sufficient to decompose them. If a precipitation occurs, as is the case with ferric salts, &c., the solution is titrated with the precipitate in it. Ferrous salts may with advantage be previously oxidised.



Porcelain dish and round burner.

In titrating the solution is kept steadily boiling by means of a round burner; an ordinary Bunsen would cause bumping. The baric chloride solution is run in, in quantity known to be insufficient, and 3 or 4 c.c. of the assay withdrawn with a pipette and filtered through a fine filter-paper into a test-tube. Add a drop or two of baric chloride, and judge from the appearance of the precipitate how much more of the standard solution may be safely run in. Towards the finish add half a c.c. at a time to the assay, and filter off a portion after each addition. It is best to have the test-tubes arranged in order on a stand and to continue the addition of the standard until half a dozen portions for testing have been drawn off. These are tested with dilute sulphuric acid, and that tube which shows the first appearance of a precipitate marks the point at which the titration is complete. With a little practice one can judge whether a quarter c.c. should be deducted from this reading. There is no chance of accepting a false finishing point if the titration is overdone and read back.*



The following are a few examples of determinations made in this way, mainly on crystallised minerals:—

	Sulphur found.	Theoretical.
Pyrites, dissolved in acids	52·9%	53·33%
Chalcopyrite, fused with nitre ..	34·7	34·91
Chalcocite, „ „ ..	20·6	20·17
Mispickel, dissolved in acids ..	18·7	19·63
Barytes, fused with fusion mixture,	13·6	13·73

The following are of crystallised salts:—

Copper sulphate	12·8%	12·83%
Magnesium sulphate	13·0	13·01
Zinc sulphate	11·2	11·15
Ferrous sulphate	11·6	11·51

The following are some determinations on burnt ore, comparing results got by this method with gravimetric work:—

Percentage of Sulphur.

Volumetric.	Gravimetric.
2·52	2·45
5·98	5·84
3·62	3·53
4·40	4·43

In these for the volumetric determination 5 grms. of the ore were fused with 5 grms. of nitre.

These experiments were carried out in the first instance with the objects of saving labour and getting at a satisfactory method of treating mineral sulphides. The separation of globules of sulphur during solution, the interference of nitric acid and nitrates, and the nicely drawn conditions required for getting a pure precipitate of baric sulphate have made the gravimetric determination troublesome. With this process the determination of sulphur in any sulphide may be made in an hour, and the conditions of the assay allow of considerable variation without affecting the results. It yields not merely proportional but theoretical results, since the standard of the baric chloride solution may be calculated from the quantity of the crystallised salt weighed up.

In conclusion, we have to thank Messrs. Seth Clarke and Bailey, and more especially Mr. J. H. Grant, for their care in performing the greater number of the experiments.

Camborne, January 11, 1889.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Continued from p. 34).

THE discussion of the Report of the Committee on Phosphoric Acid being in order, it was directed that the method for the coming year provide for the use of Schleicher and Schüll No. 589 filters, 9 c.m. in diameter, in the determination of soluble phosphoric acid, and that the preliminary washing be by decantation from a beaker, using small quantities of water, as described by Messrs. Gascoyne and Voorhees, who considered the use of the pestle only necessary with the very high grade phosphates in New England.

After some argument the use of a pump in determining soluble phosphoric acid was left to the judgment of the analyst.

Dr. Gascoyne then called attention to the method of Isbert and Stutzer for the estimation of phosphoric acid, and gave the following determinations comparing it with the official method. The method was carefully followed,

* If the first test shows the assay to be already overdone a measured portion of a standard solution of a sulphate may be added (and subsequently deducted) and the titration continued.

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

except that half normal sulphuric acid and caustic soda were used, and cochineal as the indicator.

	Association method.	Isbert and Stutzer's method.
Acid phosphate	16·10	16·03
South Carolina phosphate	26·43	26·58
Tankage	11·16	11·19
Steamed bone	30·15	30·07
Ammoniated superphosphate	10·72	10·68
Acid phosphate, total	15·77	15·74
Acid phosphate, soluble	9·63	9·57
Acid phosphate, insoluble	2·26	2·20

He also called attention to the time required for the complete precipitation of the molybdic acid and magnesia precipitates.

The following table is the result of some experiments on this subject. The phosphate was dissolved in the usual manner, filtered, ammonia added in slight excess, acidified with nitric acid, heated to about 80° or 85° C., the molybdic acid solution added, and the solution well stirred. In the first set of experiments the molybdic precipitate was allowed to stand for five minutes, filtered magnesia mixture added, and allowed to stand two hours. In the second set the molybdic precipitate was filtered in ten minutes. In the third set the molybdic precipitate was allowed to stand one hour, and the magnesia precipitate for fifteen minutes. In the fourth set the magnesia precipitate was allowed to stand thirty minutes. In the fifth set the molybdic acid precipitate stood five minutes, and the magnesia precipitate fifteen to twenty minutes.

(Acid phosphate containing 15·82 by the official method).

Molybdic precipitate five minutes, magnesia precipitate two hours	15·78
Molybdic precipitate ten minutes, magnesia precipitate two hours	15·80
Molybdic precipitate one hour, magnesia precipitate fifteen minutes	15·80
Molybdic precipitate one hour, magnesia precipitate thirty minutes	15·82
Molybdic precipitate five minutes, magnesia precipitate fifteen to twenty minutes	15·79

	Official method.	Molybdic precipitate five minutes, magnesia precipitate 15 to 20 minutes.
Acid phosphate, total	16·10	16·07
„ soluble	10·22	10·24
„ insoluble	2·12	2·08
Ground bone	22·14	22·17
Tankage	9·93	9·90

The report was then adopted and the committee directed to insert the modifications in the method.

Refractive Index of Butter Fat.

By H. W. Wiley.

Heretofore very little attention has been given to the refractive index of butter fat in studying the properties of that substance. Having had occasion this year to examine the refractive index of various fats and oils used in the adulteration thereof, I extended the examination to twelve samples of butter fat from butter bought in the open market. The object of the investigation was twofold: First, to determine the mean refractive index; and second, the rate of variation of the refractive index for rise or fall of temperature. It is, of course, obvious that the refractive index of butter cannot be read after it solidifies, and therefore the minimum temperature at which the refractive index can be determined is not much below 30°, although the butter fat may be kept some time even at 25° without solidification. A very warm room where the temperature was reasonably constant was selected in the determination of the refractive index at the lower temperature. For the higher temperature the hot room of a Turkish-bath establishment was used. The temperatures at which the reading was made and the observed index of refraction, the rate of variation for each degree for each sample, and the mean rate of variation for each degree of the twelve samples are given in the following table:—

Number.	To.	Index.	Rate for each degree.
1	32	1·4535	0·000169
	54·6	1·4497	
2	31·9	1·4535	0·000165
	56·2	1·4495	
3	31·8	1·4530	0·000194
	55·0	1·4485	
4	30·8	1·4530	0·000146
	54·8	1·4495	
5	32·3	1·4530	0·000153
	55·8	1·4495	
6	33·2	1·4535	0·000203
	55·4	1·4888	
7	32·2	1·4540	0·000186
	56·6	1·4495	
8	32·4	1·4540	0·000157
	54·8	1·4505	
9	32·2	1·4536	0·000158
	55·0	1·4500	
10	31·8	1·4530	0·000164
	56·2	1·4490	
11	31·6	1·4540	0·000186
	56·8	1·4493	
12	31·8	1·4528	0·000171
	56·2	1·4485	

The reading of the instrument with distilled water at 18° = 1·3305. Having determined the rate of variation for butter fats in order to reduce the reading to any standard temperature, it is simply necessary to use the mean factor and add or subtract the result of the multiplication as the case may be. For instance, take the case of the first sample. The refractive index at 32° is 1·4535; suppose it is wished to reduce this to a temperature of 25°; the difference in temperature between 32° and 25° is 7°, the mean rate of variation for each degree is 0·000171, for 7° it would be 0·001197. Since the index of refraction would be higher at 25° than at 30° we add this number to the number obtained above. Then 1·4535 + 0·001197 = 1·4547 = index of refraction of that sample at 25°. The index of refraction of butter fat is distinctly lower than that of cotton-seed oil, lard oil, olive oil, and linseed oil. The rate of variation for change of temperature is also less for that of butter fat than the substances mentioned.

Dr. Farrington called attention to the fact that water was as suitable for washing the yellow molybdate precipitate as ammonic nitrate.

Isbert and Stützer had observed this, and Dr. Gascoyne said that his experience confirmed it.

On motion, the committee on phosphoric acid was directed to insert this as an alternative in the methods.

Dr. Crampton, in the absence of the chairman, Professor Rising, presented the report of the committee on fermented liquors, as contained in the following letter:—

Office of State Analyst,
Berkeley, July 18, 1888.

Dear Sir,—I hope you will not think that I have intentionally been wanting in respect to the other members of the committee on "fermented liquids" because I have till now failed to communicate with you. Early in the year we began some original work upon artificial colours, &c., and it was my expectation to have had some results that I could have submitted to you for your approval before the close of the year, but our work was interrupted by other analyses, and at the last moment the results were not sufficiently satisfactory to offer to the public. However, I believe we are on the right track, and that we

may yet be able to recognise many of these artificial colours in a very short time. I had until a few weeks ago fully expected to have been present at the August meeting of the asssociation. I had planned to have spent a few weeks in your laboratory before the annual meeting, and then and there we could have made up our report. This was my plan, but at the last moment I find myself unable to carry it out, and now am unable to make any suggestion. If the association would grant us another year I would promise to be on hand, and I think I could also promise to spend some time in your laboratory, when we could perfect our report. However, if you can make a report I would not in the least hamper you, but wish you to feel at liberty to do so. I have written Professor Wiley and Mr. Clifford Richardson my views, which are intended as an explanation to the association for the failure on my part to do my duty in the matter.

We have proved beyond all question, as I think, the presence of boracic acid in many unadulterated California wines. In addition to the test with turmeric paper we have obtained the flame-test so decided that there can be no doubt. I have just received a new spectroscope, and I shall hope by its aid to settle this point beyond all question. Our method of work is as follows:—50 c.c. to 100 c.c. of wine are evaporated in a platinum dish, ignited, and burned to ash. Part of this ash is transferred to a platinum spoon; such a one as is used for blowpipe work answers very well. A few drops of the strongest H_2SO_4 (I have used a 96—98 per cent acid), then alcohol is added, and then lighted and immediately blown out, and re-lighted and again extinguished. The first flash will show the acid very distinctly if it is present.

The adulterations that we have had to look for have been easily detected. The wine in all cases was taken direct from the wine-maker. It was taken upon its sale to the wine-dealer, who had required a certificate of purity before accepting it. Naturally, only pure wine or wine that was believed to be pure would be offered. The only kind of adulteration believed to have been practised by wine-makers is, first, the use of antiseptics, salicylic acid, sulphurous acid, and boracic acid, colouring matters, alkalies (K_2CO_3) to neutralise excess of acid, &c. The watering of wine (stretching) belongs to the dealer's art, &c. We have not had occasion to investigate this branch of the subject. We examine for plaster, bases added, antiseptics, artificial colours, copper, lead, zinc salts, alcohol, free acid (volatile and non-volatile), solid residue, ash (soluble and insoluble), alkalinity of the soluble portions, sugar, glucose, glycerin, &c., tannic acid, cream of tartar, &c. Some samples of eastern wine were clearly "manufactured."

I have been obliged to go into the country on account of my family, and am now in the midst of the Napa Valley wine region and am making the acquaintance of the wine men here, and hope to gain their confidence so that they will consult me in regard to their troubles, &c. There is a strong sentiment among the wine-makers against the use of any agent that could be called an adulterant, and I find them very anxious to maintain the reputation they already have for purity. The wine-dealer is the man we have to fear; he is ready to do almost anything and to get ahead of the chemist if he can. The Viticultural Commission has sent a special agent to Paris. They have instructed him to go about and get as many of the practices of wine-makers and dealers as possible. I find great difficulty in getting a set of samples of wine-colouring substances. They are only sold in original packages, &c., under various names. I shall hope through our special agent to get a pretty complete set, and then if I can identify them and give them their true scientific names, we will have a surer base to stand upon.

I regret that I cannot attend the meeting this year. If the convention will continue the committee I think we can get to work very early the coming year, and present to the next convention a valuable contribution to the subject. May I ask you to present my apology to Professor Fellows. I do not know his address, nor can I get it till I return to Berkeley.—Very truly yours,

W. B. RISING.

REPORT OF THE COMMITTEE ON POTASH.

The committee on the determination of potash would respectfully submit: That since the last meeting of this association little has appeared in chemical literature relating to the determination of potash, so far as we know, which calls for notice here. The method of Lindo as modified by Gladding appears to give universal satisfaction. The New Jersey Agricultural Experiment Station (Report for 1887, p. 175) has determined the potash in forty-eight mixed fertilisers by this method, with certain slight modifications, and also by the Stohmann method. The greatest difference in the results in any case was 0·27 per cent; the average difference 0·08 per cent. In two-thirds of the determinations the differences were not over 0·10 per cent, and in only one case was the difference over 0·15 per cent. Stohmann's method gave on the average slightly higher results than the other. The modified Lindo-Gladding method used at the New Jersey station is as follows:—

"The solutions were made as described in the (official method), but previous to the addition of ammonium hydrate 1 c.c. of ammonium oxalate was added; the solution was then filled to the mark, thoroughly mixed, and filtered; an aliquot part was transferred to a porcelain dish of approximately 60 c.c. capacity. From this dish the material was not removed until the double salt of potassio-platinic chloride was ready to be brought upon the Gooch filter. After the determination was removed from the bath the precipitate was moistened with water, and then washed with 80 per cent alcohol till all traces of platinic chloride were removed. It was then washed with the saturated ammonium chloride solution recommended. It was found in this laboratory that better results could be secured by adding this solution to the precipitate in the porcelain dish, and washing by decantation until all salts other than the potassio-platinic chloride were removed. Since a relatively small amount only of the potassio-platinic chloride is necessary to saturate the ammonium chloride solution, these washings were all rejected, the time saved and the greater accuracy secured compensating for the loss of larger amounts of the solution.

"After this washing has been completed, the double salt was transferred to the Gooch filter, washed with pure alcohol, dried, and weighed. The salt was then dissolved in hot water, and the final weight of the potassio-platinic chloride secured by difference."

The Report being open to discussion, Dr. Gascoyne called attention to the recent experiments of Lindo contained in CHEMICAL NEWS, lvi., 103, approving the Association's methods.

Professor Scovell said he had some difficulties, and Mr. Richardson spoke of the presence at times, in the case of superphosphates, of sulphate of lime in the final double salt.

Mr. Voorhees then described the modification practised at the New Jersey Agricultural Experiment Station, as given in the Eighth Annual Report, p. 175, and said that they found the Lindo-Gladding method most desirable when a little oxalate of ammonia was used to remove lime, and the evaporation was not carried too low, and referred to the large series of results which he had published in the Report referred to.

If the evaporation were carried too far, solids might form which would be insoluble in alcohol, in which case a small quantity of water should first be added, and then the strong alcohol. The greatest error in inexperienced hands lies in this point.

Mr. Chazal said he had also found error in not evaporating low enough.

Mr. Voorhees called attention to the fact that the presence of ammonia in the air of the laboratory pro-

duced no effect with the Lindo method, as the ammonia double salt would afterwards be dissolved out by the wash, and then moved the addition to the Association method of the use of oxalate with the ammonia and evaporation to dryness with HCl, taking up with water, repeated evaporation, and taking up with alcohol.

Report of the Committee on Nitrogen.

Your Committee on Nitrogen have the honour to present the following Report of the work which has been accomplished during the year:—

Abstract of Articles which have Appeared during the Year on the Determination of Nitrogen in Fertilisers.

(Compiled, by request, by Dr. E. H. Jenkins, Connecticut Agricultural Experiment Station, and A. M. Peter, Kentucky Agricultural Experiment Station.)

The Kjeldahl Method.

Lenz (*Fres. Zeitschr. Analyt. Chem.*, xxvi., p. 590) has tested the effects of omitting oxidation with potassium permanganate after boiling the substance to be analysed with sulphuric acid. He used a flask of 100 c.c. capacity, 0·2 to 0·7 grm. of substance, 10 c.c. oil of vitriol, and 5 grms. metallic mercury. The boiling was continued until the substance was clear and colourless. In one series of determinations no permanganate was added; in another it was added as recommended by Kjeldahl. In all cases higher results were obtained when permanganate was used; generally the differences were small, but in some cases amounted to 0·33 per cent.

Ulsch (*Zeitschr. für das Gesammte Brauwesen*, 1887, p. 3; *Fres. Zeitschr.*, xxvii., 73) calls attention to the fact that if platinum chloride is added to hasten oxidation when the substance is boiled with oil of vitriol, as recommended by him in a previous paper, an excess must be avoided. Too much platinum chloride retards, instead of hastening oxidation, and if the boiling is continued too long, platinum may destroy ammonia by "catalytic action," and so cause loss of nitrogen. He also recommends the use of iron sulphate to destroy mercuro-ammonium compounds formed when mercury is used to hasten oxidation. It has the advantage over potassium sulphide that it can be added to the acid before neutralising it, thus avoiding danger of losing nitrogen.

Dafert (*Landwirtschaft. Versuchs-St.*, xxxiv., 311; also *Fres. Zeitschr. für Analyt. Chem.*, xxvii., 222) has studied the chemical reactions involved in the method, and the question how generally applicable the original method of Kjeldahl is, and whether it can be so modified as to make it available for determining nitrogen in all classes of compounds. His conclusions are briefly as follows:—

(1). Sulphuric acid withdraws from the nitrogenous organic matter the elements of water and of ammonia, and from them forms ammonia.

(2). The sulphurous acid which is evolved regularly reduces the nitrogenous compounds; but this effect is insignificant compared with that mentioned above.

(3). The addition of organic compounds (sugar, &c.) to nitrogeneous matters delays the formation of ammonia, except in cases where it changes a nitrogenous substance, which is volatile or easily decomposed, into one which is less easily attacked by sulphuric acid.

(4). Potassium permanganate, when brought into the hot mixture, destroys the organic compounds still remaining. A part or all of the nitrogen in such compounds forms ammonia. In quantitative work, when the previous digestion with acid has been carried far enough, and the permanganate is added carefully, all the nitrogen is thus converted into ammonia.

(5). His study of the effect of adding metals or metallic oxides leads to the conclusion that the addition of a metal to a substance which is easily oxidised, or is easily decomposed by sulphuric acid, may cause loss of nitrogen by a too rapid oxidation during the formation of ammonia, and in this way the process is shortened by sacrificing accuracy. Only in special cases, where the substance is very stable, is it safe to use platinum chloride to hasten oxidation, as recommended by Ulsch.

(6). He finds that nitrogen can be accurately determined by the original Kjeldahl method in all amides and ammonium bases, pyridin and chinolin bodies, alkaloids, bitter principles, albumenoids, and allied substances; also, most likely, in the indol derivatives.

In the following substances nitrogen can not be determined satisfactorily by Kjeldahl's original method.

All nitro-, nitroso-, azo-, diazo-, hydrazo-, and amidoazo- bodies, compounds of nitric and nitrous acids, the hydrazines, and probably cyan-compounds.

For the determination of nitrogen in these classes of compounds probably no general rule can be given, but the peculiarities of each group must be studied as Jodlbauer has studied the special modifications required by nitrates.

E. Waller and H. C. Bowen (*Jour. Analy. Chem.*, xi., 293) give a sketch of the history of the method, and mention modifications which they have adopted, containing nothing essentially new, except that they evaporate off most of the sulphuric acid used in the oxidation of the substance, and heat some time after adding the permanganate, an operation which seems hazardous. To the paper is appended a list of the papers which have been published on the Kjeldahl method.

The New Jersey Agricultural Experiment Station (*Report N. J. Expt. Sta.*, 1887, p. 169) has compared, in the case of nineteen fertilisers, the results obtained by the modification of Kjeldahl's method as described by Scovell with those obtained by the absolute method as described in the "Report of the Connecticut Experiment Station" for 1879. The results showed very satisfactory agreement. The largest difference was 0·14 per cent; the average difference, 0·06 per cent; in eight cases the absolute method gave on the average 0·05 per cent more nitrogen; in eleven cases the modified Kjeldahl method gave on the average 0·06 per cent more nitrogen.

E. H. Farrington (*Report Conn. Expt. Sta.*, 1887, p. 126) reports comparative determinations of nitrogen in thirty-four samples of mixed fertilisers containing nitrates by the Jodlbauer-Kjeldahl method and the absolute method as described in the reports of the same station for 1878 and 1879. His conclusions are as follows:—

"An inspection of these results shows that in 68 per cent of the cases the difference between the two methods was not over 0·1 per cent, and in 88 per cent of the cases not over 0·15 per cent. The greatest difference was 0·21 per cent."

"The plus differences are 14 in number, the minus differences 20. The average of the former is 0·066, of the latter 0·085. It is evident, then, that the two methods are about equally accurate."

Otto Shönherr (*Chem. Zeit.*, xii., 217) applies the azotometer to the Kjeldahl determination. The digestion flasks are graduated by a mark on the neck to a convenient volume (150 c.c.), and after the oxidation has been effected in the usual way the contents of the flask are diluted, neutralised approximately, made up to the mark, and mixed, and an aliquot part (50 c.c.) decomposed in the azotometer with 50 c.c. hypobromite solution. Results accurate.

R. Meldola and E. R. Moritz (*Jour. Soc. Chem. Ind.*, vii., 63) purify sulphuric acid from ammonium sulphate by adding about 0·05 grm. potassium nitrate per 10 c.c. to the acid and heating about two hours.

(To be continued).

Experiments on the Action of Various Phosphates in the Cultivation of Cereals.—J. Raulin.—The author concludes that, at least under the conditions of his experiments, insoluble native phosphates may be utilised, like superphosphates and precipitated phosphates, provided they are employed in the first year in a proportion five to six times larger.—*Comptes Rendus*, cviii., No. 1.

OBITUARY.

PROFESSOR BRAZIER.

Mr. James S. Brazier, F.C.S., Emeritus-Professor of Chemistry in Aberdeen University, died at his residence, 17, Bon Accord Square, on the afternoon of the 14th inst., heart disease being the immediate cause of death. It was the rapid development of this ailment that led to his retirement from office last year, and since that time he has more or loss suffered. In June last he had, under the care of his medical adviser, Dr. Angus Frazer (one of his old students and assistants), to be removed from Alford, whither he had gone for change of air, and he has not since been able to leave the house. His death, therefore, which occurred at five o'clock on Monday, January 14, was not unexpected, and the end came peacefully.

Mr. Brazier's connection with the Medical School of Aberdeen commenced thirty-six years ago, when, in 1852, he was appointed assistant and substitute to Dr. Clark, Professor of Chemistry in Marischal College. He was a native of Rye, Sussex, was educated in King William's College, Isle of Man, and, in 1847, entered the laboratory of the Royal College of Chemistry, London, where he soon attracted the special attention of Professor Hofmann by the perseverance and earnestness with which he prosecuted his studies. His remarkable skill and dexterity in the performance of experiments rapidly carried him through the Course, and in time he rose to be Senior Assistant in the College. After this he accepted an offer made to him by Professor Andrews to become Chemical Assistant in the laboratory of Queen's College at Belfast, from which town he came to Aberdeen, as has been said, in 1852, succeeding Dr. John Smith, who had been appointed to the Chair of Chemistry in Sydney, for which appointment Mr. Brazier too had been an applicant. He continued as Dr. Clark's substitute till the union of the Colleges in 1860, when that gentleman retired. Professor Fyfe, of King's College, then succeeded to the Professorship in the University, but, as that gentleman never lectured, Mr. Brazier discharged the duties of the chair. On Dr. Fyfe's death in 1862 Mr. Brazier received the well-merited promotion, and he resigned the Fordyce Lectureship, which he had held since 1853.

The promise of professional distinction given by Mr. Brazier in his earlier days was amply fulfilled. Though not a medical man he was a brilliant chemist. As a lecturer it has been said of him that perhaps he was not quite so clear as a beginner would like, sometimes overrating the power of his students to follow him into the intricacies. But as an experimenter he could hardly have been surpassed—one authority saying that in this department "he was so felicitous as to be unrivalled," and another that the "class of practical chemistry was one of the best Courses in the University." The Professor's method of letting each student do the testing required for himself is said to be a special feature of this school. It was well for the University in those days that it had a man of such talent on its staff. Whoever else may claim credit, none will deny, as Principal Geddes said of him when his retirement was announced, that he exerted a powerful influence on the development of the Medical School, whose high reputation it was ever his aim to maintain. With colleagues and students alike Mr. Brazier was a great favourite. In their weekly journal, *Alma Mater*, the latter, in an appreciative article, truly characterised him as "a popular professor," and at the close of last summer session, when the intelligence of his retirement was announced, the students presented him with an address of sympathy. The secret of his popularity with them was said by their organ to lie in this—

"That he is a gentleman in every sense of the word, and consequently he treats his students as gentlemen. There is not a word, not an act, of his which can be recalled, that clashes with this description, and, among the many pleasant memories we will carry with us through the world of Aberdeen and Aberdeen University, one of the most pleasing will certainly be the hearty ringing laugh of Professor Brazier."

Apart from his duties as a teacher, Mr. Brazier did other important work for the University. For many years he acted as Secretary to the Medical Faculty and for the examinations for the Degree, and he succeeded to the office of Dean on the retirement of Dr. Ogston. His promptitude, accuracy, and courtesy in all matters of business were on many occasions acknowledged by his colleagues. With affairs outside the University he did not take much concern, but for many years he held the office of gas analyst to the Corporation of Aberdeen, and was for a time Chairman of the Laundry Company. The labours of his Chair prevented him from contributing to the literature of his profession, but in his earlier days he published, as the result of his own researches, several papers, the most important of which were an "Analysis of the Mineral Constituents of the Flax Plant, and of the Soils on which the Plants had been Grown," an "Analysis of Plate Glass," and the results of a series of experiments on two organic acids.

Mr. Brazier, who was in his 63rd year, married his cousin, Miss Russell, by whom he is survived, as also by their family, which consists of three sons and two daughters. All the sons are in the Customs service of the Chinese Government, and the eldest is at home at present on furlough. Deceased was connected with St. Paul's Episcopal Church, of which he was a manager.—*Aberdeen Journal.*

NOTICES OF BOOKS.

Water Analysis: A Practical Treatise on the Examination of Potable Water. By J. Alfred Wanklyn and Ernest Theophron Chapman. Seventh Edition; by J. Alfred Wanklyn, M.R.C.S., Corresponding Member of the Royal Bavarian Academy of Sciences, &c. London: Trübner and Co.

The treatise before us is not a simple re-issue of the last edition, but contains some important additions. Part I., describing the "ammonia" process for water analysis, together with the ordinary accessory determinations required in the examination of drinking-waters, has undergone no alterations. We find an account of the "moist combustion process"—the method for the determination of the organic matter in water, which was patented by the author some time ago. We do not intend to re-open the discussion on this unusual step. But it might, we think, have been a convenience if an account had been given of the permanganate process as now practised and recommended by Dr. Tidy, so that the chemist might the more conveniently satisfy himself whether the strictures on the top of p. 54 are justified. It would be interesting, further, to see Mr. Wanklyn's estimate of the Girardin process, which turns not upon a determination of the oxygen required to burn up all the organic matter present, but of that remaining dissolved in the water and supposed to decrease progressively with the readily oxidisable impurities. This process, however, is more applicable to polluted streams and the effluents from the treatment of sewage than to drinking-waters, properly so-called.

Under the heading "Poisonous Metals" we are glad to see instructions for detecting traces of chromium. The soluble compounds of this metal are at once so formidable and so extensively used in the arts that their absence in the drinking-waters of the manufacturing districts ought to be fully ascertained. At the end of this chapter the author makes the very justifiable remark that London has, perhaps, had a most fortunate escape in the collapse

of the great scheme for bringing water to it from the Lake District of Cumberland. We may here add "or from any metalliferous region."

It is an important question in how far the new water supply of Manchester, obtained from Thirlmere, is blameless in this important respect. We have never heard the present water supplied to the cotton metropolis, derived from the Woodhead Valley, impeached on this score. At the same time we know that in making the Woodhead railway-tunnel very important deposits of galena were found, which were practically ignored because their working would have interfered with the traffic on the line.

The author has a favourable opinion of filtration, on the large scale, as a means of dealing with organic pollutions.

The second part of the work treats of the specific gravity of natural waters and the precautions to be taken in its determination; of the carbonic acid present; of the residues, soluble and insoluble, left on the evaporation of the water; on hardness, the general quantitative analysis of residues, and on gases and vapours held in solution. Carbonic acid appears, in some waters at least, to form a considerable item. In the water supplied by the West Middlesex Company it amounts to no less than 11·9 grains per gallon. Mr. Wanklyn does not consider that the nitrates and nitrites furnish a trustworthy measure of the defilement of water. The question of phosphates is noticed in this edition. The author considers that "much nonsense has been talked about phosphates in drinking-water, and the fact has been overlooked that, except as infinitesimal traces, they cannot exist along with carbonate of lime in a clear water." This contention can scarcely be disputed. But in practice the analyst may meet with waters containing no carbonate of lime, and in such the proportion of phosphates may throw a useful light on the degree of animal pollution.

Under "Purification of Waters" Mr. Wanklyn discusses distillation, filtration, and precipitation by lime. His opinion on filtration, if properly conducted, is very favourable. The Clark process he decidedly recommends as removing not mere hardness, but to a considerable extent organic matter. Precipitation by means of alum is mentioned as having been used by the Chinese in the case of the river Peiho. In reality it has been used by that nation for time immemorial in all cases of foul—rather than hard—waters.

For the examination of sewage, industrial waters, and sewage-effluents no particular directions are given. This is also, perhaps, the proper place to remark that we find no reference to the use of the microscope in the examination of waters. Mr. Wanklyn's opinion would here, doubtless, have been of value.

The third part of the treatise contains examples of complete mineral analyses, notices of the water supply of London, and of other important towns, and an appendix, largely controversial, which the author thinks may serve "for the encouragement of all such as are suffering persecution for the sake of truth."

Mr. Wanklyn is by no means disposed to join in a crusade against the London Water Companies. He considers that even Thames water, as taken at places above the metropolis, may be, and actually is, purified by filtration to such an extent as to compare not unfavourably with municipal water supplies drawn from purer sources. On the other hand, he considers it a fortunate circumstance that London is not largely supplied with hard waters, rich in calcium and magnesium sulphates, like that furnished by the Kent Company. We believe that in districts supplied with such water the death-rate from diarrhœa has been found to be on the average higher than in parts using, *e.g.*, filtered Thames water.

We do not suppose that any chemist who practises water analysis will omit to add this new edition to his library.

CORRESPONDENCE.

BLOWPIPE ANALYSIS.

To the Editor of the Chemical News.

Sir,—In the review of Colonel Ross's book on the blowpipe it is stated that blowpipe analysis is still untaught at the Royal School of Mines; and then the remark is made "if there is here no mistake this is a fact much to be regretted."

May I be permitted to say that as long as I was connected with the School of Mines as much blowpipe work was done by students commencing chemistry as the limited time of the chemistry course for Associate Students allowed. We were not able to take the ordinary run of students through such a complete course of instruction in the blowpipe as that indicated in Colonel Ross's comprehensive book; but, in a good many cases, where a student had more than the usual short time at disposal, or was interested in mining or mineralogy, or likely to take up mining as a profession, much attention was given to blowpipe work; and, I believe, in some cases, even Colonel Ross's book was consulted and worked by.

I have not heard that instruction in the use of the blowpipe has been cut out of the chemical course since I left the school.—I am, &c.,

W. R. Hodgkinson.

Royal Artillery College, Woolwich.

DETECTION OF BLOOD.

To the Editor of the Chemical News.

Sir,—A sample of human blood, taken from the heart of a victim of "fuel gas" poisoning, still shows, after an interval of two years, all the characteristics noted at the time of the autopsy. The bottle in which it is contained has been frequently opened for purposes of examination.

Odour of decomposition has developed, of course, but the vivid redness, lack of coagula, and absorption bands peculiar to carbon-monoxide poisoning, still remain.—I am, &c.,

W. P. Mason.

Rensselaer Polytechnic Institute,
Troy, Jan. 9, 1889.

SOLUBILITY OF BRASS.

To the Editor of the Chemical News.

Sir,—In this month's number of the *Journal of the Chemical Society* is a paper by Mr. S. U. Pickering on "The Principles of Thermo-chemistry," in which (p. 17) he mentions incidentally, as an illustration of his argument on a thermo-chemical point, that brass dissolves in weak sulphuric acid.

Having been hitherto unaware that this was the case, and having been unable to find reference to it in such books as I have consulted, I should feel obliged if Mr. Pickering would say whether the statement is based on the result of his own observation, or has been recorded as a fact by others, and in the latter event indicate where it is to be found.

Bertram Blount.

Laboratory, Broadway, Westminster,
Jan. 22, 1889.

INDIAN INK.

To the Editor of the Chemical News.

Sir,—I find that a colour apparently identical to Indian ink can be produced by the action of sulphuric acid on camphor.

An excess of camphor should remain some twenty-four hours in strong sulphuric acid; it then results in a gelatinous mass of a slighly reddish colour. This, when heated, effervesces, gives off fumes of sulphurous acid, and turns intensely black. By evaporation the superfluous sulphuric acid and camphor (for there remains an excess of both, the weakened acid not acting on the camphor), can be driven off. The remainder when applied to paper as a paint appears, to my unartistic eye, to be Indian ink.

When dissolved in water it remains an indefinite time without precipitating. It appears to be dissolved, not held in suspension.—I am, &c.,

B. Piffard.

Hill House, Hemelhempsted,
Jan. 11, 1889.

SEXTON'S INORGANIC CHEMISTRY.

To the Editor of the Chemical News.

Sir,—A few days ago I received from the publishers (Blackie and Son), a copy of a new text-book on Inorganic Chemistry, by Professor A. Humboldt Sexton, F.R.S.E., F.I.C., F.C.S. Uhder the heading "Nitric Oxide" the following statements occur:—

"*Composition.*—The composition of the gas may be determined by exactly the same method as described for nitrous oxide."

"*Difference from* O *and* N_2O.—Leaves half its own volume of N on explosion with H."

On turning to "Nitrous Oxide" I find the methods given for the determination of its composition are:—

(1). "By burning Na in a measured quantity of the gas."

(2). "A quantity of the gas is measured in a eudiometer over mercury, excess of H is added, and an electric spark is passed."

It is, of course, easy enough to distinguish nitric oxide from oxygen, or nitrous oxide; but Professor Sexton, by saying how he would burn sodium in nitric oxide, or explode that gas with an excess of hydrogen, would, perhaps, confer a favour on others of your readers, besides

A Benighted Teacher.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cvii., No. 27, December 31, 1888.

Action of Sulphuretted Hydrogen upon Zinc Sulphate in a Neutral or Acid Solution.—H. Baubigny.—This paper will be inserted in full.

The Determination of Manganese by Means of Hydrogen Peroxide.—Ad. Carnot.—A correction to the author's last paper on this subject. The salt of manganese employed in his experiments is not the dioxide, but the saline compound, $5MnO_2,MnO$.

Preparation and Properties of Ferric Orthose.—P. Hautefeuille and A. Perrey. — This paper is rather of mineralogical than of chemical interest.

Preparation and Properties of Methyl Fluoride and of Isobutyl Fluoride.—H. Moissan and H. Meslans.—The reaction of silver fluoride upon the methyl, ethyl, propyl, and butyl fluoride easily yields fluoric ethers, which have not hitherto been studied. They possess a great stability, and are less readily saponified than the corresponding chlorine compounds. As far as the butyl fluoride they are gaseous; fluorine, when substituted for chlorine in the molecule, greatly lowers the boiling-point.

New Method for the Assay of Alcohol Founded on the Action of the Amines upon the Aldehyds.—Ch. Girard and X. Rocques.—If a mixture of aldehyd and of metaphenylene-diamine hydrochlorate are heated together in an alcoholic solution the liquid takes an orange-red colour, which increases on agitation, and a splendid green fluorescence is developed. On adding ammonia the colour turns to a yellow and the fluorescence disappears. The authors proceed as follows:—They dissolve in 200 c.c. of alcohol at 50 per cent, 3 grms. of metaphenylene-diamine hydrochlorate, and boil for half an hour with a reflux condenser. The liquid takes a light yellow tint. It is let cool for half an hour and agitated a little towards the end of this time. The colour of the liquid darkens, and if aldehyd is present it takes a fine green fluorescence. It is then distilled rapidly, and 125 c.c. of the distillate is collected, which marks 75°. To this Savalle's test is applied, and the tints obtained are compared with those given by typical solutions of pure amylic alcohol in (ethylic) alcohol of 75°. If the amylic alcohol is present in small quantities (from 1 to 0·1 per cent) it passes over entirely in the 125 c.c. Savalle's test, which is inaccurate except aldehyd is previously removed, depends on the brown colour produced on heating alcoholic solutions of amylic alcohol with an equal volume of pure undiluted sulphuric acid.

Combination of Sodium Glycol-alcoholate with Glycol.—M. de Forcrand.—A thermo-chemical paper.

The Active Crystalline Principle Extracted from the Seeds of Strophantus glabrus, of the Gaboon.—M. Arnaud.—This highly poisonous principle, which is non-nitrogenous, and ranks not among the alkaloids but the glucosides, has received the name ouabaine, and scarcely differs from the principle extracted from the *Acokanthera*. The formula assigned to both is $C_{30}H_{16}O_{12},H_2O$.

Study of the Combustion-heats of the Terpilenols of Terpine Hydrate and of Anhydrous Terpine.—W. Louguinine.—Not susceptible of useful abstraction.

Vol. cviii., No. 1, January 7, 1889.

Reactions of Oxygenated Water with Chromic Acid.—M. Berthelot.—The author proposes a thermo-chemical explanation of the reactions recently pointed out by Ad. Carnot. He observes that the two opposite determinations of hydrogen peroxide by chromic acid and of chromic acid by hydrogen peroxide are not reciprocal. We cannot, without the risk of error, overstep the limits of the reaction and then return by means of an excess of the antagonistic reagent, as it can be done with permanganate. The use of a notable quantity of one of the two reagents added at once in a proportion sufficient for the complete reaction is admissible in very dilute liquids on account of the slowness of the reactions. But in strong solutions this method of operating might occasion at certain points the presence of a momentary excess of the reagent and change the character of the reaction.

Butylic Ethers, Mixed, and properly so-called.—E. Reboul.—This memoir does not admit of useful abridgment.

A Contribution to the Study of the Ptomaines.—Oechsner de Coninck.—The author has converted the ptomaine $C_8H_{11}N$ into pyridin, and the intermediate product, carbono-pyridin, presents the principal characters of nicotianic acid.

The Determination of Organic Nitrogen by Kjeldahl's Method.—L. L'Hote.—The author considers it unnecessary to insist upon the accuracy of the soda-lime process. Analysts know that its results are irreproachable if we take care not to heat too strongly, so as to avoid the dissociation of the ammonia, and if the soda-lime in fine powder is intimately mixed with the substance

under examination. His researches show that, contrary to what has been asserted, the figures yielded by the Kjeldahl process are lower than those furnished by soda-lime. All the organic nitrogen does not reappear in the sulphuric acid in the state of ammoniacal nitrogen.

The Forage Legumens on Acid Soils.—Paul de Mondesir.—The author does not question the beneficial action of limestone on leguminous forage plants. But he concludes from his experiments that if these plants find in the soil phosphates and potash they can content themselves, as far as lime is concerned, with the proportion existing in combination with the humic matters.

MEETINGS FOR THE WEEK

MONDAY, 28ht.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Egyptian Tapestry and Textiles," by Alan S. Cole.
TUESDAY, 29th.—Institute of Civil Engineers, 8.
— Society of Arts, 8. "Gold and Silver Mining in Colorado," by Thomas W. Goad.
— Royal Institution, 3. "Before and After Darwin —II. Evolution," by Prof. G. J. Romanes, F.R.S.
WEDNESDAY, 30th.—Society of Arts, 8. "The Construction of Photographic Lenses," by Conrad Beck.
THURSDAY, 31st.—Royal, 4.30.
— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
FRIDAY, Feb. 1st.—Geologists' Association, 8. (Anniversary).
— Royal Institution, 9. "The Life-History of a Marine Food-Fish," by Prof. W. C. McIntosh, F.R.S.
SATURDAY, 2nd.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.

THE LONDON GEOLOGICAL FIELD-CLASS LECTURES on the "THAMES VALLEY," by PROFESSOR H. G. SEELEY, F.R.S., in Holborn Town Hall, Gray's-Inn Road, every Wednesday Evening from February 6th to the 27th, at 8 o'clock. Tickets, 5s. each for the Course, may be had from W. Wesley and Son, 28, Essex Street, Strand, W.C.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE METROPOLITAN BOARD OF WORKS will meet at the office of the Board, Spring Gardens, S.W., on Friday, the 8th day of February, 1889, at 12 o'clock at noon precisely, and will then be prepared to open TENDERS by parties who may be willing to CONTRACT for the SUPPLY of 1000 tons of MANGANATE OF SODA, to be delivered at the rate of 100 tons per week, from the 18th of March next. Parties desirous to submit tenders may obtain a copy of the specification, form of tender, and information as to places of delivery on application to the Chemist of the Board, at the office, Spring Gardens, between the hours of 9 a.m. and 4 p.m. (on Saturdays between the hours of 9 a.m. and 2 p.m.), until Thursday, the 7th day of February, 1889. The tenders, which must be on the form supplied from this office, and addressed to the Clerk of the Board, are to be delivered at the office before 4 o'clock on the last-mentioned day, and no tender will be received after that hour. The parties tendering must be in attendance at the Board at 12 o'clock on the day appointed for opening tenders, and any tender which is not fully filled up in every particular will be rejected. The Board do not bind themselves to accept the lowest or any tender.

J. E. WAKEFIELD, Clerk of the Board.
Spring Gardens, S.W., 18th January, 1889.

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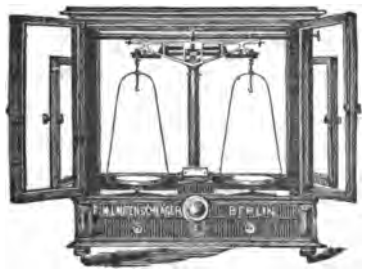

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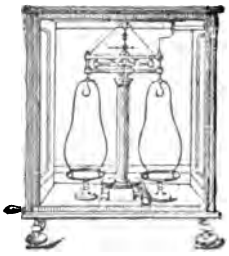

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THE CHEMICAL NEWS.

Vol. LIX. No. 1523.

THE VOLUMETRIC ESTIMATION OF COBALT IN PRESENCE OF NICKEL, MANGANESE, AND OTHER METALS.

By NORMAN McCULLOCH.

In the writer's inquiry on the more likely methods hitherto suggested for the volumetric estimation of cobalt in the presence of nickel (Chemical News, vol. lvi., p. 27) it was shown that the processes were inherently valueless, and justifying the so far exclusive use of gravimetric methods for accurate work. The inquiry, in fact, constituted in part a corroboration of Bayley's analyses of the higher oxides of nickel and cobalt (Chemical News, vol. xxxix., p. 81), and in so demonstrating the unstable and indefinite character of cobaltic hydroxide as ordinarily obtained precluded the idea of accepting the "available" oxygen of this compound as a means to the exact estimation of cobalt.

But, the writer now finds, peroxide of cobalt in cyanide solution, so to speak, is of stable and definite composition, and in the determination of the oxygen necessary to convert cobaltocyanide to cobalticyanide, there is a ready means to the exact estimation of cobalt in presence of nickel, manganese, and other metals.

Cobaltocyanide exhibits, in its affinity for oxygen, powerful reducing properties, determining the complete or partial reduction of many metallic oxides, and, in the case of chromic acid, robbing it of one half of its oxygen, so:—

$$6CoCN_2+24KCN+2CrO_3+3H_2O= \\ =3Co_6(CN)_{12}Co_2+Cr_2O_3+6KHO.$$

Further, the above reducing effect of a metallic cyanide or chromic acid is peculiar to the cobalt compound, and not materially exhibited by other cyanides. It follows, then, from the foregoing, that the reduction of chromic acid in cyanide solutions is an indication of the presence of cobaltocyanide, and, by the indirect estimation of the reduced chromate with standard ferrous salt, quantitatively applicable to the estimation of cobalt.

Thus indicating the process to be described, the necessary apparatus and standard reagents are sufficiently familiar, and it will suffice to touch on the following:—

Standard Normal Bichrome (49·17 grains in 10,000 grains H_2O) should be delivered from a burette graduated to fifths of a division (1 div. = 10 grains) 1 div. = 0·059 grain cobalt.

Standard Ferrous Salt—($FeSO_4NH_42SO_4+6H_2O$).—This reagent is standardised with bichrome in the usual way, and best on such quantity as is used in the estimation.

Potassium Cyanide Solution of any convenient strength, and, in the author's case, a five per cent solution of very pure cyanide (95 per cent), and of this solution, 12·5 divs. theoretically sufficed for one grain of cobalt. The cyanide solution may be standardised by delivering into a hot aqueous solution of 3 grains pure sulphate of nickel until the precipitate first formed is re-dissolved, and considering the quantity so consumed *plus* one half more, as equivalent to 1·14 grains of cobalt in the process.

Apparatus.—An arrangement is required for effecting the reaction of the cobaltocyanide with the chromate in absence of air and at the boiling-point; and it may consist simply of a 12 oz. flask fitted in the neck with a double holed cork, one hole for reception of thistle funnel, the other for escape of vapour. The tail end of the funnel should dip beneath the surface of the liquid in flask, and its mouth be somewhat constricted.

The Estimation.—The standard bichrome and cyanide solutions are conveyed in their proper quantities to the flask above described, a few drops of ammonium hydrate added for subsequent neutralisation of any free acid in solution to be tested, and the whole diluted, if necessary, to a convenient bulk with water.

The amount of bichrome taken need not *greatly* exceed the theoretical requirement for the greatest probable quantity of cobalt to be estimated, but, with the cyanide, an allowance is made also for the conversion to soluble double cyanides of such other metals as may be present.

The cork and thistle-funnel are now placed in position, and the solution boiled to expel air from the flask. The hot solution to be tested, of convenient bulk and not too acid, and free, of course, from oxidising or reducing constituents, is now added, and the ensuing reaction is instantaneously complete.

After this stage the continued use of the cork and thistle-funnel is necessary only in presence of manganese.

The contents of the flask are now cautiously treated with excess of a moderately warm concentrated solution of ammonium chloride, and the ebullition sustained for about ten minutes longer to expel volatile cyanide (an operation conducted in acid chamber or in a draught of air to carry off poisonous fumes).

In digression, the stronger acids may not substitute the ammonium salt, as tending to reduce chromic acid in presence of hydrocyanic acid, and particularly *insoluble* cyanide.

It is now left, preceding the estimation of non-reduced chromic acid with ferrous salt, to throw down soluble cobaltocyanide and decompose potassium-nickel cyanide by the addition of nickel sulphate. This is to prevent the subsequent formation of ferrous cobaltocyanide and double cyanide of iron and nickel respectively—compounds difficultly soluble in dilute acid—and, consequently, low results. To effect the above precipitation, a weight of nickel is required at least equal to that of the nickel and cobalt existing in the contents of the flask, but if such acids as arsenic and phosphoric are present more is needed, as their precipitation is involved. Simply, the solution of nickel is added until no further precipitate is formed, or until the precipitate settles in a peculiar manner to be known by experience; great excess of nickel is thus avoided, which would tend to interfere with the ferricyanide reaction in the subsequent operation.

It now only remains to pour the contents of the flask into excess of a hot aqueous solution of standard ferrous salt contained in a basin, acidify with a few drops of hydrochloric acid, and titrate with bichrome in usual way in order to complete the estimation.

The cobalt is calculated by multiplying the difference between the number of divisions bichrome taken at the outset of the estimation and that found at the completion by 0·059 grain and correcting this by a slight allowance for reducing action of the potassium cyanide and its impurities on the chromate. In the author's case this correction has been taken from the experiments of Table I., and it has been deemed sufficiently near to accept the reducing action of the cyanide as simply proportionate to the quantity of this reagent used in the estimation, although it is not altogether independent of the proportion and amount of the bichrome, the degree of dilution, length of time of boiling, &c. The subjoined table shows that 100 divs. of the bichrome boiled for a few minutes with its own bulk of the cyanide, and then for about ten minutes more with addition of excess ammonium chloride, loses in value to the extent of about one division. One division, then, has been deducted from the amount of bichrome reduced by the cobaltocyanide in such estimations, using the above bulk of cyanide, a fifth of this for 25 or 30 divs., and so on. It is, of course, advisable, where the highest accuracy is desired, to determine the necessary correction by a blank experiment, and duplicating also the approximate quantity of cobalt.

TABLE I.

Divs. std. $K_2Cr_2O_7$ taken.	Divs. KCN solution used.	Grains std. ferrous salt used.	Divs. std. $K_2Cr_2O_7$ consumed.
100	—	40	1·0
100	—	40	1·2
100	100	40	1·9
100	100	40	1·8
100	100	40	2·2
100	10	40	1·4
10	100	5	3·6

Table II. shows results of volumetric estimations of cobalt alone, and in presence of nickel, manganese, lead, phosphorus, and arsenic respectively. The figures of the fourth column have been submitted to correction on basis already described.

TABLE II.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains CO found.
3·62 Co	70·0	80·0	60·8	3·59
1·14 ,,	25·4	25·4	19·2	1·13
1·14 ,,	25·4	25·4	19·3	1·13
0·07 Co+3·80 Ni	3·0	50·0	1·3	0·07
1·14 ,, +2·28 ,,	25·0	50·0	19·1	1·12
0·03 ,, +2·28 ,,	2·0	25·0	0·4	0·02
0·73 ,, +2·28 ,,	16·0	40·0	12·5	0·73
5·42 ,, +1·14 ,,	98·0	120·0	91·5	5·40
1·08 Co+6·80 Mn	25·0	30·0	18·4	1·08
0·36 ,, +1·36 ,,	10·0	10·0	5·9	0·34
0·36 ,, +1·36 ,,	10·0	15·0	6·1	0·36
1·08 ,, +2·27 ,,	25·0	30·0	18·3	1·08
1·08 Co+1·65 Pb	25·0	20·0	18·5	1·09
0·91 Co+0·57 P	25·0	20·0	15·5	0·91
1·08 Co+5·13 As	25·0	30·0	18·2	1·07
1·08 ,, +1·54 ,,	25·0	30·0	18·4	1·08

Estimations have been made in presence also of aluminium, zinc, antimony, molybdenum, and uranium with perfectly satisfactory results. The process, though, is not applicable in presence of copper. Cuprous cyanide is formed, and cyanogen liberated, which converts its equivalent of cobaltocyanide to cobalticyanide, and the cuprous cyanide is not completely oxidised by the ferric chloride in the final operation of the process. Consequently the results are too low (*vide* Table III.), and copper must not be present in any solution in which it is proposed to determine cobalt by the volumetric process described in this Paper.

TABLE III.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains CO found.
1·08 Co+0·05 Ca	25·0	25·0	17·8	1·05
1·08 ,, +0·10 ,,	25·0	25·0	17·3	1·02
1·08 ,, +0·05 ,,	25·0	25·0	17·8	1·05

The experiments of Table IV. have been devoted to studying the influence of iron.

TABLE IV.

Grains of cobalt and other substances taken.	Divs. std. $K_2Cr_2O_7$ used.	Divs. KCN solution used.	Divs. std. $K_2Cr_2O_7$ reduced.	Grains Co found.
1·08 Co+0·45 Fe	25·0	30·0	18·1	1·06
1·08 ,, +0·45 ,,	25·0	40·0	17·5	1·03
1·08 ,, +0·90 ,,	25·0	40·0	17·9	1·05
1·08 ,, +0·90 ,,	40·0	25·0	18·1	1·06
1·08 ,, +0·90 ,,	50·0	25·0	18·0	1·06
1·08 ,, +0·90 ,,	50·0	50·0	18·2	1·07
2·17 ,, +0·90 ,,	50·0	50·0	35·4	2·08
0·10 ,, +0·15 ,,	3·0	8·0	1·0	0·06
2·17 ,, +0·15 ,,	50·0	50·0	36·1	2·13
2·17 ,, +0·90 ,,	70·0	50·0	36·2	2·13
3·62 ,, +0·15 ,,	90·0	70·0	62·0	3·65

Ferric hydroxide readily oxidises cobaltocyanide in presence of excess cyanide to cobalticyanide, and is itself converted to ferrocyanide. A soluble chromate checks this action as being the more ready oxygen furnisher, but, nevertheless, the tendency of the results is to come out beneath the truth.

It will doubtless be best to separate iron as well as copper, and in the case of a cobalt ore the author would dissolve the sample in aqua-regia, and evaporate to dryness. The nitric acid would then be destroyed by twice or thrice evaporation to dryness with hydrochloric acid, and the copper precipitated from the solution of the residue by sulphuretted hydrogen. In the filtrate from sulphide the iron would be separated by the acetate of *soda* method, and the iron precipitate re-dissolved and re-precipitated in a similar way to separate any small portion of cobalt. The combined filtrates from the acetate precipitates would be evaporated to convenient bulk, and the excess of acid neutralised by caustic or carbonated soda. The solution so obtained would then be added to suitable amounts of bichrome and cyanide in a manner that will now be understood, and the estimation completed volumetrically. Thus, in the author's opinion, may cobalt be determined in its ores, &c., with an accuracy to be surpassed and a convenience to be approached by no other known analytical procedure.

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ON SOME NEW TESTS FOR TANNIC AND GALLIC ACIDS.

By S. G. RAWSON, B.Sc.

THE ordinary reagents which are used in detecting these acids are ferric chloride, which gives its well-known reaction with both, and a solution of gelatin which reacts only with tannic acid. In the case, however, of a dilute solution of tannic acid no precipitate is obtained with gelatin; and hence considerable difficulty arises in distinguishing between the two acids. Young's test for these acids, viz., potassic cyanide, I found to work well, giving a reddish colour with gallic acid and none with tannic acid.

If a solution of tannic acid be treated with ammonium chloride alone a precipitate falls, but only with extreme slowness; whereas on the addition of ammonia a beautiful white precipitate instantly appears, but this, probably by oxidation, becomes rapidly of a reddish brown colour. With gallic acid no precipitate falls in either a strong or a weak solution, but the liquid becomes of a red colour. In a solution of tannic acid containing one part of tannic acid in 5000 of water a precipitate falls, but slowly, and with more dilute solutions, therefore, it is better to drop the mixture of ammonic hydrate and chloride very cautiously on to the top of the tannic acid solution. Where the two liquids come in contact with one another the white precipitate makes its appearance at once in a well-marked line. This white line is distinctly visible in a solution of tannic acid containing 1 part in 20,000 of water. If, however, a piece of black paper be held behind the tube the delicacy of the test is increased and 1 part in 50,000 parts of water may be now detected. There is no advantage in substituting other ammonium salts such as the phosphate, carbonate, or oxalate for ammonium chloride.

With gallic acid, as previously mentioned, no precipitate is formed; but a ring, usually of a greenish colour on its lower surface, is produced, this being recognisable in solutions containing 1 part of gallic acid in 100,000 of water.

Some few experiments were tried, in the case of tannic acid, with a view to using the method as a quantitative one; but owing to the unstable nature of the precipitate

in alkaline solutions, this attempt was, as I anticipated, a failure.

Another delicate test for both gallic and tannic acids is to add to the solution containing one of them chlorine water and then ammonia, a beautiful red colour being at once produced. With tannic acid the colour is very well marked and distinct, but is not quite so noticeable with gallic acid, for with this acid, as is known, ammonia alone gives a red colour. With a mixture of potassic ferricyanide and ammonia both acids also give a dark red coloured solution. In the case of tannic acid 1 part in 10,000 of water gives a distinct red colour to the whole of the solution. In a weaker solution, say 1 part in 30,000 of water, the red colour is best seen by looking down the test-tube through the whole column of the liquid. In still more dilute solutions, containing only 1 part tannic acid in 100,000, of water it is better to compare the tint, which is now more of a yellowish brown, with the tint of a blank experiment, *i.e.*, one containing the same amount of ammonia and of potassic ferricyanide in the same volume of water, but with no tannic acid present. Under these conditions the change in colour will be perfectly apparent, and the delicacy or the reaction may be carried considerably further. The red colouring matter can be salted out, and I am at present engaged on some further investigations into its composition and properties.

University College, Liverpool.

ACTION OF SULPHURETTED HYDROGEN UPON ZINC SULPHATE IN NEUTRAL OR ACID SOLUTIONS.

By H. BAUBIGNY.

If we pass a current of sulphuretted hydrogen through a saturated solution of zinc, says Berzelius in his celebrated treatise, a part of the metal is precipitated, but when the liquid becomes acid up to a certain point the action ceases.

Thus expressed the fact is exact. But on generalising it for all cases, as it has been subsequently done, we have formulated a law which is false, and is entirely at issue with experience, especially if the liquids are dilute.

In principle every solution of zinc sulphate or chloride (taken in the state of neutral salts), made in the proportion of 0·3 grm. of the salt to 100 c.c. of water, no longer contains zinc if, after being treated with a current of sulphuretted hydrogen at the ordinary temperature (20°), it is left for some hours in a closed vessel.

If the weight of zinc is doubled for the same volume of liquid the precipitation seems at first less perfect. Still, after the lapse of five hours, the liquid contains merely 0·004 to 0·006 grm. of the salt used, and if the action is prolonged, not filtering off the sulphide until the expiry of three days, the mother-liquor does not contain more than 0·001 grm.

In the simplest case, that of a neutral liquid, the reaction is produced similarly with the chloride and the sulphate. Hence, as it is the more easily procured and weighed in a state of purity, the author has exclusively employed it in his experiments.

In a liquid acidified with sulphuric acid, in the case of zinc sulphate, the phenomenon preserves its general course; zinc sulphide is not formed at first, but, after a certain time, the shorter the less free acid is present, the liquid becomes turbid, small traces of sulphide are formed, and the precipitate increases gradually.

Zinc sulphate in an acid solution behaves like neutral nickel and cobalt sulphates (*Comptes Rendus*, xciv., pp. 1183 and 1251 and cv., pp. 751 and 806). With 0·3 grm. of the salt to 100 c.c. of the liquid it was necessary to add sulphuric acid to the extent of about thirty times the acid present in the salt in order that in such a solution saturated at 0° with sulphuretted hydrogen no action shall ensue on leaving it in a closed vessel at the ordinary temperature. But if we apply heat the rise of temperature diminishes the solubility of the sulphuretted hydrogen, and consequently increases its tension so that a decomposition of the zinc salt takes place, and there is a formation of sulphide, the weight of which increases progressively. The case is very distinct at 100°. At this temperature the action of the zinc salt is annulled only if we add a weight of free acid 90 or 100 times greater than the acid existing in combination with the salt.

The multiplicity of the conditions which intervene in the transformation of zinc sulphate into sulphide gives for every case a different result, varying with these conditions.

Thus experience confirms that the weight of free acid to be added to a given and constant weight of zinc sulphate to annul the action of sulphuretted hydrogen decreases with the volume of water in which the salt is dissolved. Inversely, in a given acid liquid (*e.g.*, 7·5 grms. SO_3 in 100 c.c.) and saturated with sulphuretted hydrogen at 0°, nothing will be produced if the weight of the dissolved sulphate is 0·150 grm., even if we heat to 100° in a closed vessel; whilst the conversion of the sulphate into sulphide will take place gradually, even at the common perature, if the weight of the salt is increased to 1·500 grms.: and this transformation will reach such a limit that the weight of the sulphate remaining undecomposed will be decidedly lower than 0·150 grm.

Thus, the results vary with the conditions of the experiment, and for the decomposition of zinc sulphate by hydrogen sulphide there can be no question, properly speaking, of a limit depending on the degree of acidity of the liquid, since the decomposition is a function not merely of the original proportion of the free sulphuric acid at the outset and of the water which serves as a solvent, but further of that of the acid and the metal present in the state of a salt, soluble or insoluble, the sulphide intervening, as the author has already shown in the case of nickel and that of cobalt.

These facts being thus established, M. Baubigny proposes to draw from them conclusions bearing on the solution of a number of analytical questions.—*Comptes Rendus*, vol. cvii., p. 1148.

UNIFORM METHODS FOR THE ANALYSIS OF FERTILISERS, CATTLE FOODS, DAIRY PRODUCTS, SUGAR, AND FERMENTED LIQUORS.*

(Concluded from p. 45).

Report of the Committee on Nitrogen (continued).

Other Methods.

Houzeau (*Pharm. Centr.*, xxviii., 627, 628, also *Jour. Analyt. Chem.*, ii., 354) proposes a mixture to be used in determining nitrogen for the conversion of nitrogen in any combined form into ammonia. Equal weights of sodium acetate and thiosulphate are melted in their water of crystallisation and allowed to solidify. The mixture is powdered and kept in well-stopped bottles. The combustion is made as follows:—In the posterior end of the combustion tube are placed two grms. of the above mixture and two grms. of coarsely-pulverised soda-lime, and then a layer of soda-lime a few c.m. long.

The finely-powdered substance to be analysed (0·5 grm. if rich in nitrogen, 10—25 if a soil) is well mixed with 10 grms. of the salt mixture and 10 grms. of soda-lime, and filled into the tube, followed by soda-lime and an asbestos or glass-wool plug. The combustion is made as usual

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

and the mixture at the rear end of the tube is used at the close of the operation for aspirating. The ammonia is absorbed and titrated in the usual way.

The New Jersey Agricultural Experiment Station (*Rep. N. J. Expt. Sta.*, 1887, p. 169) has determined the nitrogen in 140 samples of complete fertilisers, 22 samples of nitrogenous matter of high grade, and 19 samples of ground bone, both by the soda-lime method and the Kjeldahl method. The latter gave on the average 0·04 per cent more nitrogen in complete fertilisers, 0·05 per cent more in high-grade nitrogenous matter, and 0·10 per cent in bone.

Reference should also be made to an elaborate series of experiments and observations on the soda-lime method made in the laboratory of the Wesleyan University by or under the direction of Prof. W. O. Atwater (*Am. Chem. Jour.*, ix., 311; x., 111, 113, 197, 262). A complete abstract of these papers is not deemed necessary here. Prof. Atwater says in closing his paper: "The perfection to which Kjeldahl's method has lately been brought, and its accuracy, convenience, and inexpensiveness have led us to its use in this as in many other laboratories. Our experience leads us to decidedly prefer it to the soda-lime method, though we find it advantageous to use both, making one check the other. But the danger of incomplete ammonification of some classes of compounds, *e.g.*, alkaloids, makes us feel it necessary to control both by the absolute method for all classes of substances except those for which they have been most thoroughly tested."

Recommendations.

Your committee would recommend the continuance of the five methods adopted last year, viz:—

(1). The absolute method.
(2). The Kjeldahl method.
(3). The Kjeldahl method modified for nitrates.
(4). The Ruffle method.
(5). The soda-lime method.

But after a careful consideration of the results obtained above, they would recommend:

(1). That the soda-lime method be given more in detail in the hopes of obtaining more concordant results.

(2). That detail changes be made in the Kjeldahl methods.

(3). That attention be called to the use of zinc-dust in the Kjeldahl modified method. Prof. H. A. Weber calls attention to the fact that unless the zinc-dust be in an impalpable powder and well mixed into the solution, the nascent hydrogen fails to come in contact with all the nitro-compounds, and therefore reduction is incomplete.

Discussion of the report being in order, Messrs. Frear, Gascoyne, and Voorhees stated that they had found trouble with zinc-dust, blanks showing some nitrogen.

Dr. Voorhees stated that at the New Jersey Station they always made blanks for error, and questioned whether commercial chemists did so.

Professor Scovell said he had found that sulphuric acid often contained nitrogen, but the strictly C. P. from Aimer and Amend was quite free.

Dr. Voorhees then gave an account of the experiments at his station with the Scovell modification of the Kjeldahl method, as published in their last annual report, and described a convenient form of iron gas-pipe condenser. Of the soda-lime method, Dr. Gascoyne said that the necessity for absence of a channel, as shown by Atwater, was an important factor.

Dr. Voorhees pointed to the necessity of fine division of the substance to at least 60 mesh, while coarse samples could be used with the Kjeldahl method.

Professor Scovell called attention to the generally bad results on cotton-seed and blood with soda-lime in the tables given in his report, and a general opinion that a careful understanding of the details of working this method were very necessary, and without this results would easily fall too low.

With the Scovell modification of the Kjeldahl method general satisfaction was expressed by those who had tried it carefully.

Professor Stubbs then presented the Report of the Committee on Sugar, as follows:—

REPORT OF THE COMMITTEE ON SUGAR.

The increasing interest in sugar-growing in this country is manifested by the large governmental aid recently given to the manufacture of sugar from sorghum and sugar-cane. This interest has created a demand for chemical information relative to all sugar matters, from the raw juice to the manufactured articles, and to meet this demand is one of the increasing duties of this association. "A Manual of Sugar Analysis," by J. H. Tucker, published by D. Van Nostrand, New York, in 1881, contains all of the approved methods of analyses up to that date, many of which are still used without modifications in the laboratories of the world. Others have been slightly modified, while a few have been discarded as totally without merit.

In all sugars and sugar products, including raw juices, the following determinations are needed for industrial work:—

(1). Total solids.
(2). Percentage of sucrose.
(3). Percentage of invert sugars.
(4). Ash.

In raw juices.—(1). Syrups and molasses: The tota solids may be obtained in the following manner:—

(1). By accurately graduated spindles, preferably Baix.
(2). By taking specific gravity.
(3). By evaporating to dryness a weighed quantity mixed with ignited sand in a tared dish.
(4). A method (Wiley's) of trying and weighing a piece of filter paper, say 12 by 2 inches, saturating with juice or with molasses (easily disseminated over the paper by means of a few drops of alcohol), drying and re-weighing.

Of the above methods only the third is absolutely correct. The fourth in our hands gives results slightly low, while the second and first are only approximate. However, the first method, when accurately graduated spindles are used, corrections made for temperature are sufficiently approximate for industrial work. A sufficient time should elapse between the pressing of the cane and the reading of the spindle to permit all the air bubbles to escape; half an hour is time enough.

TABLE I.

Analyses of Varieties of Sorghum from Experimental Plats of Sugar Experiment Station in Louisiana, made July 12 and 13; all immature.

Number of variety from experimental plats.	Total solids by Bux.	Per cent sucrose, polarisation.		Per cent glucose.
		Single.	Double.	
1	6·8	1·0	1·81	3·40
2	7·0	2·0	2·96	1·90
3	9·8	4·8	5·78	1·59
4	6·5	0·4	2·00	3·29
5	10·9	5·4	6·90	1·82
6	9·0	2·3	3·95	2·12
7	11·7	6·0	7·50	2·13
8	10·6	4·8	6·67	2·68
9	13·3	6·9	8·81	4·25
10	8·5	2·0	4·18	3·40
11	11·1	6·2	8·89	1·70
12	8·9	0·0	1·53	6·34
14	13·2	7·0	7·78	3·71
15	13·6	8·4	9·20	2·75
16	13·3	8·3	8·95	2·85
17	11·8	4·0	5·12	3·40
18	11·5	5·2	6·22	3·30
19	9·8	2·2	3·22	2·95

No.	Where from—plantation.	Beaumé.	Sp. gr.	Total solids.	Per cent sucrose by double polariscope.	Per cent glucose.	Other solids.	Per cent sucrose by Fehling.	Total sugar as glucose.
1	Belle Chasee	41·4	1·4039	78·2	39·59	24·32	15·03	39·65	65·06
2	John Crossly & Sons ..	41·8	1·4092	79·0	41·68	22·69	14·44	40·61	65·44
3	Joseph Garr	40·6	1·3933	76·6	34·91	29·19	9·05	32·25	63·14
4	Boujere	40·7	1·3940	76·7	37·62	24·77	15·32	37·53	64·28
5	Belle-Terre	41·6	1·4065	78·6	42·57	22·78	14·63	41·30	66·26
6	Woodlawn..	42·3	1·4165	80·1	33·42	33·75	14·49	32·79	68·22
7	Crescent	42·3	1·4165	80·1	36·44	28·42	14·92	37·67	67·08
8	Mary	42·3	1·4165	80·1	38·82	26·86	16·72	39·08	67·84
9	Perseverance	43·2	1·4287	81·9	40·31	20·00	22·93	43·54	65·84
10	David	42·3	1·4165	80·1	37·62	26·92	16·72	36·97	65·84
11	Orange Grove	42·4	1·4179	80·3	42·25	26·73	13·05	39·94	68·78
12	Palo Alto	42·6	1·4205	80·7	38·14	25·96	16·43	40·28	68·36
13	Hester	42·5	1·4192	80·5	34·72	30·17	18·52	33·14	65·06

Sucrose.—For sugars, raw juices, and syrups sucrose is best determined by a simple polariscopic test with the following precautions.

(1). Proper sampling of substance.

(2). Careful weighing of sample.

(3). Avoid excess of sub-acetate of lead.

(4). Dissipate bubbles, which prevent accurate gauging by a drop or two of ether.

(5). Perfect filling of polariscope tube.

(6). Careful reading of polariscope.

(7). Making all tests in duplicate.

(8). Testing the accuracy of polariscope daily. Instead of direct weighing of substance the Ventzke's process may be used. Following the above (see Tucker, pages 261 and 262), all ripe sorghum juices, all sugars, and syrups of above grade give accurate results. With immature sorghum juices double polarisations show increased results. (See Table I.).

With molasses of all kinds, at least from Louisiana cane, simple polarisation gives results always too low, especially if during the process of manufacture much sugar has been inverted. Double polarisation by Clerget's method of inversion is then usually used for determining the sucrose in these bodies, and when invert sugar is the only optically active body, is approximately accurate. When optically active bodies other than invert sugar are present, recourse must be had to inversion and estimations by Fehling's or Violette's methods. Tuchsmidt has confirmed the accuracy of Clerget's process, and Reichardt and Bellman have perfected it, giving us what is now known to us as Clerget's method.

Creydt, on the other hand, has corrected the constant 144 of Clerget, and substituted therefore 142. He further prescribes HCl of 1·1888 specific gravity, equal to 38 per cent of acid, and washes with this acid the bone charcoal used for filter, dries, and pulverises it. Herzfeld thinks the exact truth as to this constant is not yet known on account of the difficulties; first, of maintaining the temperature of observation; second, the nature of the so-called "pure sugar" used. Landolt recently adds other errors, among others, 1° Ventzke (white light) = 0·34455 circular degrees (sodium light) is too high, and that diverse active substances give numbers sensibly different. He has found with Dr. Rallyan for 1° Ventzke (white light). Sucrose = 0·3465, dextrose = 0·3448, invert sugar = 0·3433 circular degrees. Landolt finds the constant of Clerget to be 142·4, an expression believed to-day to be the most exact. Herzfeld gives a perfected Clerget method which has the following differences:—Water of local temperature surrounds the tube, which cools the solution, at once permitting accurate reading of temperature. The use of washed and dried bone-black after Reichardt and Bellman, and calculation of results according to the formula of Clerget, modified by Landolt, viz:—

$$R = \frac{100\ S}{142{\cdot}4 - \frac{1}{2}T}$$

The table of work (see above), carefully done by my assistant, Prof. W. L. Hutchinson, with molasses from different plantations in Louisiana, shows results by double polarisation and inversion and estimation with Fehling's solution.

While the concurrence of results in the main are satisfactory, there are some which could not be made to agree, suggesting strongly either a fault in the method or other optically active bodies than invert sugar, perhaps both; and while for the present we recommend Clerget's method we earnestly request an investigation of Herzfeld's modification of Clerget's method during the coming year by all sugar chemists.

Invert Sugar.

The exact estimation of invert sugar in sugar matters has been recently ably investigated and discussed. Heretofore invert sugar has been determined by a simple titration with the cupric tartrate liquor of Fehling, Violette, &c. The formulæ for the preparation of these solutions are numerous. They all contain sulphate of copper, rochelle salts, and caustic alkali, and present little real difference. Meissl and Herzfeld have described a process based upon the weight of copper reduced from the Fehling solution when accompanied by particular conditions. In spite of its great precision it has found only limited application, especially in France, where its numerous difficulties have prevented its use on an extensive scale. Beggart employs Fehling's solution, which he keeps in bottles (bouchées á l'èmeri), and which are placed in a dark place. To titrate this liquid they dissolve 0·95 grm. of pure sugar in a little water with 2 c.c. of hydrochloric acid, and after adding 500 c.c. of water it is gently heated for ten minutes at 70° C. This solution is cooled and saturated with bicarbonate of soda and raised to one litre; 0·25 c.c. of this liquid will reduce 5 c.c. of Fehling's solution, the end reaction being determined as usual by means of ferrocyanide of potash and acetic acid, using Wiley's tubes.

To preserve a standard solution of invert sugar he prepares a 15 per cent solution and made strongly alkaline. In this way it will be preserved many months. With this solution he daily tests his Fehling's solution. This constitutes the only merit of this process, a merit which should be observed in every process using the cupric tartrate process.

Patterson's process is based upon another principle. To 100 c.c. of Fehling's solution he adds a quantity of sugar insufficient to precipitate all the copper, and determines excess of copper by a titration with a normal invert sugar solution containing 0·002 grm. per c.c. Herzfeld rightly condemns the process, since no correct conclusions from the use of the cupric tartrate solution can be drawn without considering the strength of ebullition and influence of crystallisable sugar upon the reducing power of invert sugar.

All the copper liquids so far proposed, although different in composition, have one common property, viz., they all contain a salt of copper, a double tartrate of

potash and soda, and caustic or carbonated alkali. They are all reduced not only by invert sugar but also by dextrine and sometimes even by sucrose. After a certain time they undergo alteration, deposit the oxide of copper, especially if exposed to light.

Soldaini's solution does not possess these objectionable qualities, at least so says Degener, who has studied carefully its properties.

This liquid is prepared, according to Degener, in the following manner:—(1) 40 grms. of sulphate of copper is dissolved in water, and, in another vessel, 40 grms. of carbonate of soda is also dissolved in water. The two solutions are mixed and the copper precipitated in the state of hydrobasic carbonate according to following equation:—

$$2CuSO_4+2Na_2CO_3+H_2O= \\ =CuCO_3CuOH_2O+CO_2+2Na_2SO_4.$$

The precipitate is washed with cold water and dried. This precipitate (15 grms.) is added to a very concentrated and boiling solution of bicarbonate of potash (about 415 grms.) and agitated until the whole is completely, or nearly so, dissolved, water is added to form a volume of 1400 c.c., and the whole mass heated for two hours upon a water-bath. The insoluble matter is filtered, and the filtrate, after cooling, is of a deep blue colour, and has a density of about 22·5° (Baumé (1·185). The sensibility of this liquid is so great that it gives a decided reaction with 0·0014 grm. of invert sugar. The presence of sucrose in the solution increases still this sensibility. Ammoniacal salts are not hurtful to the reaction, but they do sometimes retain in solution a slight quantity of copper.

It is then indispensable to boil the solution for five minutes at least in order to drive off ammonia. The quantitative test for sugar is made in the following manner:—Fifty c.c. of Soldaini's solution is boiled for five minutes upon a water-bath, and 15 c.c. of the sugar liquid (containing 100 grms. of matter in 100 c.c. of water) added, and boiled again for five minutes. After a rapid cooling the liquid is thrown upon a Swedish filter and washed with water until every trace of a blue colour disappears. Then the paper is removed and the precipitate examined, which should be of a clear red colour.

Bodenbaender and Schiller (*Zeitschrift des Vereins fur Rubenzucker-Industrie*, 1887, p. 138) have determined the following quantitative process with this liquid:—100 to 150 c.c. of Soldaini's solution is placed in an Erlenmeyer flask and heated for five minutes over a gas jet. A solution containing 10 grms. of sugar (clarified with subacetate of lead if necessary) is added, and heated again for five minutes, always over a direct flame. This precipitates all the copper, to which is added 100 c.c. of distilled water, in order to cool the mass very quickly. The troubled liquid is filtered (preferably through a Sohxlet or Herzfeld filter) and washed with distilled water. This oxide of copper is reduced in a current of hydrogen, and the copper is weighed in a metallic form, and this weight multiplied by 0·3546 gives the weight of invert sugar. By this method 0·01 per cent of invert sugar can be accurately determined.

Sidersky has recently offered a new volumetric method, based upon the use of Soldaini's solution. With sugars the same method as is now in use with Fehling's solution can easily be followed, watching the disappearance of the blue colour, and testing the end with ferrocyanide of potash and acetic acid. This process offers no serious objections common to Fehling's solution, but is inapplicable to coloured sugar solutions, such as molasses, &c. For the last the following is recommended:—25 grms. of molasses are disssolved in 100 c.c. of water and subacetate of lead added in sufficient quantities to precipitate the impurities, and the volume raised to 200 c.c. and filtered. To 100 c.c. of the filtrate are added 25 c.c. of concentrated solution of carbonate of soda, agitated, and filtered again. 100 c.c. of the second filtrate with excess of lead removed is taken for analysis. On the other hand, 100 c.c. of Soldaini's solution is added to a flask of Bohemian glass and heated five minutes over an open flame. The sugar solution is now added little by little, and the heating continued for five minutes. Finally, the heat is withdrawn and cooled by turning in 100 c.c. of cold water, and filtered through a Swedish filter, washed with hot water, letting each washing run off before another addition. Three or four washings will generally remove completely the alkaline reaction. The precipitate is then washed through a hole in the filter into a flask, removing the last trace of copper. 25 c.c. of normal sulphuric acid is added with two or three crystals of chlorate of potash, and the whole gently heated to dissolve completely the oxide of copper, which is transformed into copper sulphate, according to equation—

$$3Cu_2O+6H_2SO_4+KClO_3=6CuSO_4+6H_2O+KCl.$$

The excess of sulphuric acid is determined by a standard ammonia solution (semi-normal), of which the best indicator is the sulphate of copper itself. When the deep blue colour gives place to a greenish tinge the titration is completed. The method of titration is performed as follows:—Having cooled the contents of the flask, a quantity of ammonia equivalent to 25 c.c. of normal sulphuric acid is added. From a burette graduated into one-tenth c.c. standard sulphuric acid is dropped in drop by drop, agitating after each addition. The blue colour disappears with each addition to reappear after shaking. When the last trace of ammonia is saturated the titration is complete, which is known by a very feeble greenish tinge. The number of c.c. is read from the burette, which is equivalent to the copper precipitated. The equivalent of copper is 31·7, and the normal acid equivalent is 0·0317 of copper. Multiplying the copper found by 3546 we have the invert sugar. A blank titration is needed to accurately determine the slight excess which gives the pale green tinge. This process is to be highly recommended if experiments show it to be as accurate in our hands as it has in France.

(4) *Ash.*—For the determination of ash, Scheibler's process of ignition with H_2SO_4 and deducting one-tenth is recommended. For details, see Tucker's "Manual," p. 226.

Your Committee, in conclusion, recommends that for technical work the following is admissible:—

(1) Taking the total solids with an accurately graduating Brix spindle and correcting for temperature.

(2) A polariscopic test for raw juices, low syrups, and sugars, using the precautions mentioned in this Report.

(3) For heavy syrups, molasses, and tank bottoms, double polarisation with Clerget's tables.

(4) For invert sugar use Fehling's or Violette's solutions, preferably the last, using as an end reaction ferrocyanide of potash and acetic acid; best accomplished by use of Wiley's tubes.

(5) Ignition with sulphuric acid at a low red heat and deducting one-tenth for ash.

For laboratory work the above may be substituted by some of the more accurate methods given above.

Remarks on Professor Stubbs's Report.

By H. W. Wiley.

In connection with the Report of Professor Stubbs on sugar analysis, wuich has just been presented to the Association, I beg leave to call the attention of the members to a standard polariscope which I have had constructed by Schmidt and Haensch in Berlin. This instrument is the double compensating apparatus manufactured by that firm, which has already gained great favour among chemists. The apparatus which I show you was specially constructed for the use of this Department, and is capable of receiving an observation tube 600 m.m. in length.

By means of the double compensating apparatus any

error which may be due to an inaccuracy in the quartz wedge is reduced to a minimum. The apparatus has the advantage of using ordinary lamp-light, which is of great importance when outside-station work is to be considered, where the difficulty of securing a monochromatic flame is great. This instrument has lately been examined by Professor Andrews, the expert employed by the United States Treasury to investigate the methods of sugar analysis employed in the United States custom-houses. He proved it to be as nearly exact as any instrument can be made. It is not necessary to mention that for general purposes of research a rotation instrument like the large model Laurent is preferable to any form of compensating apparatus; but in sugar work, where an arbitrary scale is used, I think an instrument of this kind would be found superior to anything now in use.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1889.

Mr. WILLIAM CROOKES, F.R.S., President, in the Chair.

MESSRS. Arthur G. Bloxam, T. O. Sandell, and Walter Tate were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John William Clayton, Blackburn; Philip Norman Evans, Nash Mills, Hemel Hempstead; Robert Ferguson, M.A., Burgh School, Linlithgow, N.B.; John Joseph Hickey, Beech Mount, Harpurley; William Hall Jowett, Blackburn; William Eggleston Lauer, Chemisches Laboratorium, Georgen Strasse 35, Berlin; George McAlman, 246, Bath Street, Glasgow; Harry East Miller, 1264, 14th street, Oakland, California, U.S.; Arthur Frederick Morgan, 21, Rumford Street, Manchester; George Arthur Pingstone, Yew Bank, Brook Road, Heaton Chapel; Harry Holliss Robins, 11, Mecklenburgh Street, W.C.; James Speakman, 4, Craigisbank Terrace, Dundee; Stanley Southam, 7, Ritson Road, Dalston, N.; Thomas B. Stilleman, 358, Bloomfield, Street, Hoboken, New Jersey, U.S.A.

The following were duly elected Fellows of the Society:—Messrs. Charles Lightfoot Barnes, Percy Carter Bell, Albert Cooper, William Hepworth Dixon, Dr. Carl Duisberg, Frederick Charles Garrett, B.Sc., B. S. Gott, B.A., Robert J. Gow, Edward Gudeman, Ph.B., Allan Twistleton Hall, John A. Hall, Cecil Leigh, Lionel Remond Lenox, Ph.B., George Lloyd, Arthur Lloyd Mackeroy, M.A., James Muir, Robert Hodgson Parker, Charles W. Priestley, B.Sc., Frank R. Peace, John Percival, B.A., John Provis, Edgar Richards, Percy Andrew Ellis Richards, Siegfried Ruhemann, Ph.D., M.A., Walter Venis.

The following papers were read:—

1. "*A Cubical Form of Bismuthous Oxide.*" By M. M. PATTISON MUIR and ARTHUR HUTCHINSON.

A puce-coloured precipitate is produced by adding excess of potassium cyanide to a boiling solution of bismuth nitrate in dilute nitric acid. Boedeker (*Annalen*, cxxiii., 61) gave the formula $Bi_2O_5 \cdot 2H_2O$ to this substance; according to C. Hoffmann (*Annalen*, ccxxiii., 110), however, the precipitate is Bi_2S_3, the sulphur being derived from impurity in the cyanide; and one of the authors has described it as an oxycyanide of bismuth (*Proc. Roy. Soc. Edin.*, xi., 557). Further experiments show that the precipitate is a compound of Bi, C, N, and O. When this precipitate, without being washed, is repeatedly treated with boiling concentrated potash solution, 2—3 per cent of the bismuth in the precipitate goes into solution with practically the whole of the carbon and nitrogen, and tetrahedral crystals of bismuthous oxide remain. It is almost impossible to free these crystals from an adhering film of the puce-coloured compound by treatment with potash; very long-continued action of boiling potash—so concentrated that it solidifies on cooling—does, it is true, remove the last trace of the carbon and nitrogen compound, but the crystals are much corroded by this action. To obtain the cubical form of bismuthous oxide free from the puce-coloured compound, it is better to remove the last traces of this substance by heating for a short time to full redness in air. Cubical bismuthous oxide has the density 8·838 at 25° relatively to water at the same temperature; the relative density of the ordinary rhombic bismuthous oxide is 8·3.

2. "*Cupric Iodide and the Interaction of Iodides with Cupric Salts.*" By D. J. CARNEGIE, B.A.

By digesting cuprous iodide with iodine and water in a tightly closed bottle at 80° for a few minutes, the author has obtained solutions of cupric iodide containing as much as 0·82 grm. per 100 c.c., but has been unable to obtain cupric iodide in the solid state, either from such solutions or by other means. A well-defined basic periodide, $[CuI_2 2CuO \cdot 4H_2O]$, was obtained by digesting copper with barium iodide. The author attempts an explanation of the fact that concentrated solutions of cupric iodide are not obtainable from the interaction of soluble iodides and cupric salts, or of iodhydric acid and cupric hydroxide, in terms of (1) the affinity which iodhydric acid and iodides generally possess for iodine; and (2) the disturbance of equilibrium which the separation of solid iodine causes in a medium which holds cupric iodide in solution. He regards the usual reason given for the non-existence of cupric iodide, viz., its intrinsic instability, as probably inadequate.

3. "*Periodates.*" Part II. By C. W. KIMMINS.

The following salts are described:—

Lead Salts.—The interaction of lead nitrate and $K_4I_2O_9$ or $Na_2H_3IO_6$ results in the production of $Pb_3H_2(IO_6)_2$. When the salt was dissolved in nitric acid, and the solution was concentrated, $Pb_3(IO_5)_2$ was formed. By boiling the first salt with concentrated nitric acid, $Pb(IO_4)_2$ was produced. The salt $Pb_3(IO_5)_2$ is formed by heating $Pb_3H_4(IO_6)_2$ to 275° for four hours. These lead periodates are more or less soluble in nitric acid; the more insoluble salts are lighter in colour than the others; the more soluble salts show a tendency to take up moisture.

Iron Salts.—On treating $Na_2H_3IO_6$ or $K_4I_2O_9$ with ferric chloride, a light brown precipitate was obtained, which on drying at 100° formed a red powder, $FeHI_2O_9$; when this was boiled with nitric acid, the salt $Fe(IO_4)_3$ was produced. The ferrous salt, $Fe_5(IO_6)_2$, was obtained from $Na_2H_3IO_6$, and the salt, FeH_3IO_6, from $K_4I_2O_9$.

Copper Salts.—The green salt, Cu_2HIO_6, was obtained both from $Na_2H_3IO_6$ and $K_4I_2O_9$. On dissolving this salt in nitric acid and concentrating, a yellow salt was produced, probably $Cu(IO_4)_2$.

Nickel Salts.—No salt corresponding to HIO_4 could be obtained. The salt $Ni_3(IO_5)_2$ is greenish yellow, and $Ni_2I_2O_9$ is black and crystalline.

Cadmium Salts.—The only salt obtained was $CdHIO_5$; it is easily prepared from $Na_2H_3IO_6$, and with difficulty from $K_4I_2O_9$.

Silver Salts.—The salt $Ag_4I_2O_9$, was formed by treating $K_4I_2O_9$ with silver nitrate; by treating this with nitric

Meta-periodates. Salts of HIO_4.	Meso-periodates. Salts of H_3IO_5.	Para-periodates. Salts of H_4IO_6.	Di-periodates. Salts of $H_4I_2O_9$.
$AgIO_4 \cdot H_2O$	Ag_2HIO_5	$Na_2H_3IO_6$	$K_4I_2O_9$
$AgIO_4$	$Pb_3(IO_5)_2$	$Na_3H_2IO_6$	$K_3HI_2O_9$
$Pb(IO_4)_2$	$Ni_3(IO_5)_2$	$Ba_5(IO_6)_2$	$Ag_4I_2O_9 \cdot 3H_2O$
$Fe(IO_4)_3$	$CdHIO_5$	$Ag_2H_3IO_6$	$Ag_4I_2O_9 \cdot H_2O$
$Cu(IO_4)_2$		$Ag_3H_2IO_6$	$Ag_4I_2O_9$
		$Pb_3H_4(IO_6)_2$	$FeHI_2O_9$
		$Fe_5(IO_6)_2$	$Ni_2I_2O_9$
		FeH_3IO_6	
		Cu_2HIO_6	

	Schultz-Sellack. $B_2O_3{\cdot}H_2O{\cdot}3SO_3$.	$H_3BO_3{\cdot}3SO_3$.	Results of analyses. (1).	(2).	(3).	(4).
SO_3	73·2	79·5	78·8	79·7	78·3	80·1
B_2O_3	21·2	11·6	11·3	10·6	12·2	11·8
H_2O	5·5	8·9	9·9 (by diff.)	9·7 (by diff.)	8·9 (by diff.)	8·1 (by diff.)

acid of different degrees of concentration, other silver periodates are formed. All silver salts yielded orange crystals of $AgIO_4{\cdot}H_2O$ when heated with concentrated nitric acid.

The salts described in this and a previous paper may be classified as in Table on preceding page.

4. "*Compounds of Arsenious Oxide with Sulphuric Anhydride.*" By R. H. Adie.

This paper describes in detail the preparation of a series of compounds of As_2O_3 and SO_3; the compounds are represented by the formula, $As_2O_3{\cdot}xSO_3$, where, $x=1$, 2, 4, and 8. $As_2O_3{\cdot}8SO_2$ is produced by the interaction of arsenious oxide and sulphuric anhydride; when fuming sulphuric acid is used, approximately $2H_2SO_4{\cdot}SO_3$, $As_2O_3{\cdot}4SO_3$, and probably also $As_2O_3{\cdot}SO_3$ are formed; $As_2O_3{\cdot}2SO_3$ is obtained by using ordinary concentrated sulphuric acid; and when acids are used approximately corresponding to the formulæ of $9H_2SO_4{\cdot}2H_2O$. $9H_2SO_4{\cdot}4H_2O$, $9H_2SO_4{\cdot}6H_2O$, and $H_2SO_4{\cdot}H_2O$, the product has the composition $As_2O_3{\cdot}SO_3$. Sulphuric acid of greater dilution than $H_2SO_4{\cdot}H_2O$ was found not to yield any compound of As_2O_3 with SO_3. All the compounds described are easily decomposed by moisture, or by heating.

5. "*On a Compound of Boric Acid with Sulphuric Anhydride.*" By R. F. D'Arcy, B.A.

On adding an excess of sulphur trioxide to boric acid, and heating the mixture until sulphur trioxide ceases to be evolved, a substance remains which is fairly stable and possesses the composition $BH_3O_3{\cdot}3SO_3$. This formula may be written $B(HSO_4)_3$, but sufficient experiments have not yet been made to determine whether the compound is a sulphate of boron or a compound of boric acid with sulphuric anhydride. In analysing the compound, use was made of Gooch's accurate method of estimating boric acid by distillation with methyl alcohol (*Proc. Am. Acad. of Arts and Sciences*, 1886—1887). Merz and Schultz-Sellack have described compounds of the formulæ $5B_2O_3{\cdot}2SO_3{\cdot}2H_2O$ and $B_2O_3{\cdot}3SO_3{\cdot}H_2O$. Attempts to obtain results similar to those obtained by these chemists were unsuccessful. The percentage composition given by the formula of Schultz-Sellack, and that given by the formula $H_3BO_3{\cdot}3SO_3$, together with the experimental numbers obtained, are stated in the Table above.

6. "*Notes on Experiments on Butter Fat.*" By A. Wynter Blyth and G. H. Robertson.

The authors have endeavoured to separate the glycerides of butter fat by (*a*) fractional crystallisation of the solid portion from alcohol; (*b*) dissolution in ether and fractional precipitation by alcohol; (*c*) electrolysis. The main result of their experiments is to show that butter fat is composed of solid crystalline fats and an oil. The proportion of the oil to the solid crystalline fats is about 45·5 of butter oil to 54·5 butter crystals. A crystalline glyceride was separated, to which the authors ascribe the formula $C_3H_5\begin{cases}C_4H_7O_2.\\C_{16}H_{31}O_2.\\C_{18}H_{34}O_2\end{cases}$

They consider that butter is mainly made up of compound and not of simple triglycerides.

To the original paper is added a note of the electrical resistance of butter fat and olive oil.

7. "*Gawalowski's Method for the Volumetric Estimation of Sulphuric Acid.*" By Barker North, Assoc. N.S.S.

In Fresenius's *Zeitschrift für Analytische Chemie* for 1888, xxvii., 152—159, is a paper on the "Volumetric Estimation of Combined Sulphuric Acid," by A. Gawalowski. As such a method is still a desideratum among chemists, I undertook, at the request of Professor Thorpe, to make a critical examination of Gawalowski's process. The method consists in adding a quantity of a standard solution of barium chloride, more than sufficient to precipitate the sulphuric acid which may be present, and titrating the excess of barium chloride with a standard solution of sodium carbonate, using phenolphthalein as an indicator of the excess of sodium carbonate.

The barium chloride solution was made as nearly seminormal as possible by weighing, and then accurately standardised by gravimetric analysis. The sodium carbonate solution was made seminormal by weighing out recently ignited Na_2CO_3. A series of experiments were made with strict adherence to Gawalowski's instructions. The errors ranged from 2 to 27·5 per cent. It will thus be seen that the method is entirely worthless. The cause of the error doubtless is the solubility of the barium carbonate, which, even in the presence of alcohol, affects the phenolphthalein to such an extent as to render it impossible to properly detect the true end point of the interaction.

8. "*Note on the 1 : 3 Homo- and the Isomeric Hetero-αβ-dichloronaphthalenes melting at nearly the same Temperature.*" By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proc.*, 1888, 104) we have specially called attention to the fact first brought under notice by one of us at the Manchester Meeting of the British Association, on September 2nd, 1887 (*B. A. Report*, 1887, 231), that *two αβ*-dichloronaphthalenes exist which melt nearly at the same temperature, slightly above 60°. Cleve, in a paper in the number of the *Berichte* issued previously in the same week as the number of the *Proceedings* containing our note, without any reference to our earlier work, corroborates our conclusion (p. 3275), but continues to assign the same melting-point (61°) to the two isomers. Cleve's earlier statement (*Ber.*, 1886, 2182) that two of the isomeric nitrosulphonic acids obtained on nitrating naphthalene-β-sulphonic acid both gave the dichloronaphthalene melting at 61° evidenced his belief, and led others to the belief, that isomeric change took place during the treatment of the sulphochlorides with PCl_5; he subsequently pointed out, however, that perhaps there were two isomeric dichloronaphthalenes melting at 61°. Our observation published in 1887 first proved that no isomeric change takes place, and thus deprived the objections which have been urged against the use of PCl_5 in determining the constitution of nitro- and sulphonic derivatives of naphthalene of their force. Erdmann, in the number of the *Berichte* just issued (1888, 3446), states that Reverdin and Nölting were the first to positively state that two dichloronaphthalenes melting at 61° exist; it is to be noted, however, that Professor Nölting was present at the meeting at which one of us brought forward the above-mentioned facts, and that Reverdin and Nölting's invaluable monograph was at that time only in the press.

In the notice referred to, Erdmann speaks of Cleve's recognition of two dichloronaphthalenes melting at 61° as an important confirmation of *his* views (*Annalen*, ccxlvii., 308) as to the stability of isomeric naphthalene-derivatives; and he states that, disregarding the changes which occur in the case of sulphonic acids when heated with water or sulphuric acid—which he has made the subject of special experimental investigation—no case is

now known of the conversion of a naphthalene-derivative into a "position-isomer." These statements afford multiple illustration of simple belief in the sufficiency of the *Berichte* and a very few other German journals as media of communication among chemists which is becoming so noticeable. The manner in which isomeric change takes place in the case of naphthalene-derivatives has been specially discussed and referred to by one of us (*Chem. Soc. Trans.*, 1887, 266, 587; *B. A. Report*, 1886, 216; 1887, 231; 1888, CHEM. NEWS, lviii., 295; *Chem. Soc. Proc.*, 1887, 143—146). A number of cases of isomeric change have been described by us, one so far back as 1881, and that, too, in the *Berichte* (1882, 204), although perhaps this case may be denied rank as one of change into a "position-isomer" by Erdmann; and we shall shortly have to describe other cases.

In the same paper Erdmann makes an acceptable addition to our knowledge in describing the synthesis of the 1 : 3-dichloronaphthalene melting at 61·5° from 1 : 3-dichlorobenzaldehyde. He, however, forgets to mention that the constitution of this dichloronaphihalene had already been determined by us: he calls attention to the existence of two dichloronaphthalenes melting at almost the same temperature as though it were an original observation; and he states that it will be his "nächste Aufgabe" to sufficiently determine the chemical differences of the two isomers in question and to discover means of discriminating between them with certainty: overlooking the fact that we have long since stated that we are engaged in further characterising the isomeric dichloronaphthalenes; and that in our recent note, to the admirable and almost verbal translation of which in that most valuable periodical the *Chemiker Zeitung* he refers and therefore has under notice, we have already described certain distinctive properties and have made the identification of the two dichloronaphthalenes in question a simple matter.

The description originally given by Erdmann and Kirchhoff of the dichloronaphthalene melting at 61·5° which they obtained from parachlorobenzaldehyde did not suffice to determine its identity, and as it was all-important to us to place the constitution of the two dichloronaphthalenes now under discussion beyond question, we have been at the pains to prepare it by Erdmann and Kirchhoff's method from parachlorotoluene. In doing this we have had cause to appreciate and value their labours. By heating the chloronaphthol with PCl_5, a product was obtained consisting of a mixture of tri- and di-chloronaphthalene: these were approximately separated by crystallising from alcohol the tri-derivative separating first in prisms melting at 120°. The residual dichloronaphthalene fused at 57—59°, and as the quantity was inconsiderable this was converted directly into sulphonic acid, from which salts and the chloride were prepared. The potassium salt was found to be sparingly soluble in water containing a little potassium carbonate, and crystallised in anhydrous scales; the sulphochloride crystallised from benzene in needles, becoming opaque on standing and melting at 117°. The dichloronaphthalene recovered from the sulphochloride by hydrolysis *melted* at 63·5°. There can be no doubt therefore that the dichloronaphthalene prepared synthetically by Erdmann and Kirchhoff's method is identical with that from Arnell's betachloronaphthalenesulphonic acid and from the betanaphthylaminesulphonic acid known as the Badische modification. Our previous conclusion that these acids are heteronucleal derivatives is thus confirmed.

Erdmann has entirely misunderstood our objections to his conclusions with respect to the constitution of the dichloronaphthalene melting at 63·5°, viz., that his method did not enable us to discriminate the 1 : 2' from the 1 : 3' modification. It is not that we think it necessary that the chlorophenylisocrotonic acid should have been isolated; our objection arises from our conviction that, as we have already said, "the origin of the hydroxyl in their acids cannot be determined." The oxygen-atom in the naphthol may be either that which originally was present in the carbonyl and which may have remained attached to the carbonyl-carbon atom; or it may be that which was contained in the carboxylic hydroxyl; or that which was contained in the aldehyde; and in the last two cases the OH-group may ultimately become associated with either of the two para-carbon atoms with which the oxygen-atom is represented as connected in the formula of phenylparaconic acid. There is at present, moreover, no valid reason to be urged against the conclusion that in some cases the OH-group may assume the one, in some other cases the other position, according to the nature of the influence exercised by the chlorine-atom. We are specially engaged with experiments in the hope of determining the exact constitution of the dichloronaphthalene melting at 63·5°.

9. "*The Constitution of Betanaphthol-α-sulphonic Acid (Bayer's acid).*" By HENRY E. ARMSTRONG.

The number of the *Berichte* just issued contains a most valuable paper by Dr. O. N. Witt, on the reduction products of the azo-dyes derived from the various naphthol- and naphthyl-aminesulphonic acids, together with another discussing the constitution of betanaphthol-α-sulphonic acid—conventionally known as Bayer's acid. In the latter I regret to say that Dr. Witt altogether misrepresents my views, misreading an early paper of mine (*Berichte*, 1880, 200); and overlooking the discussion which took place after the reading of Mr. Green's paper on November 15th last, and the conclusions arrived at by Mr. Wynne and myself with regard to the amido-acid corresponding to Bayer's hydroxy-acid published in the same number of the *Proceedings* (p. 104).

Witt speaks of my having converted Bayer's acid into 1 : 2 bromo-betanaphthol, and of my having in consequence inferred that Bayer's acid is the 1 : 2 modification; actually, however, in my paper, I describe (p. 202) the action of bromine on *betanaphthylsulphate*. I may quote the following passages from my Report to the British Association at the Manchester meeting, in 1887, read, I believe, in Dr. Witt's presence, to show what have been my views:—

"The dichloronaphthalene obtained from Bayer's modification of β-naphtholsulphonic acid is doubtless hetero-θ-dichloronaphthalene; the conclusion arrived at by Claus that this acid is a 2 : 3 derivative is not only opposed to all that is known of the behaviour of naphthalene compounds, inasmuch as it involves the assumption that on sulphonating β-naphthol the second β-position contiguous to the hydroxyl becomes displaced; it is untrustworthy, as the dichloroquinone which he obtained may have been, and doubtless was, produced by the action of chlorine liberated during the process of oxidation.

"*Theory of the Formation of Azo-dyestuffs from β-naphthol.*—It is well-known that in the case of β-naphthol itself the α-hydrogen atom contiguous to the OH-group becomes displaced by the azo-group. This position appears to be free in all the sulphonic acids which afford azo-colours, and those naphthol derivatives in which it is not free appear to be incapable of forming such colours; it is therefore a legitimate inference that all-azo-dyes derived from β-naphthol are formed by the introduction of an azo-group in the position indicated."

At the meeting on November 15th I "referred to Emmert's observation (*Annalen*, ccxli., 371) that the betanaphtholsulphonic acid corresponding to betanaphthylamine-α-sulphonic acid is convertible in a dihydroxynaphthalene different from hydrobetanaphthaquinone as incompatible with the conclusion that the α-acid was the 1 : 2 compound;" and I again expressed the opinion "that an acid in which the SO_3H and OH groups were in the relative positions 1 : 2 would not be capable of forming azo colours."

The conclusion which I had arrived at as to the probable constitution of the betanaphthol (and betanaphthylamine) azo-dyes, led me, in October, 1887, to commence their study precisely in the manner in which

Witt has now done so skilfully and with such thoroughness; at my suggestion, Dr. F. Feist reduced the benzeneazobetanaphtholsulphonic acid prepared from Schaefer's acid, and found, as Witt had done, that the reduction-product was identical with Meldola's amidobetanaphtholsulphonic acid; he obtained, by hydrolysing the acid, the known amidobetanaphthol, and converted it into betanaphthaquinone. Recently, having determined that Bayer's acid corresponded to the heteronucleal dichloronaphthalene melting at 63·5°, and that it is either a 1 : 2′ or a 1 : 3′ derivative, I had commenced the study of the *Crocéine* prepared from Bayer's acid and diazonaphthionic acid. Witt's results relieve me in a most welcome manner from pursuing the investigation. His discovery that the azo-group in the croceines is in the α-ortho-position is precisely what I had foreseen, and I have little doubt that when he examines the reduction products of the azo-dyes prepared from the other betanaphthol- and betanaphthylaminesulphonic acids, he will find that the azo-group is always introduced into the α-ortho-position contiguous to the OH-group of the naphthol, or the NH-group of the naphthylamine.

10. "*The Sulphonation of Naphthalene-β-sulphonic Acid.*" By Henry E. Armstrong.

The number of the *Berichte* just issued contains at p. 916 of the "Referate" an abstract of a patent secured by Ewer and Pick for a *new* naphthalenedisulphonic acid prepared by sulphonating naphthalene-β-sulphonic acid, or one of its salts, by means of fuming sulphuric acid. When this patent came under my notice some months ago I at once came to the conclusion that the *new* acid was the (?) β-disulphonic acid prepared by Mr. Wynne and myself by a similar process by means of chlorosulphonic acid instead of fuming sulphuric acid, and described at the meeting of the Society on November 4th, 1886 (*Chem. Soc. Proc.*, 1886, 230). On preparing the acid according to Ewer and Pick's directions this surmise proved correct. It may be added that this acid corresponds in constitution to η-dichloronaphthalene (m.p. 48°), and, therefore, to Dahl's modification of betanaphthylaminesulphonic acid. I am indebted to Mr. Garrett for assisting me to make the comparison.

At the next meeting on February 7th the following paper will be read:—

"Researches on the Constitution of Azo- and Diazo-derivatives. Part V. Compounds of the Naphthalene-β-series" (continued). By R. Meldola, F.R.S., and G. T. Morgan.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 2, January 14, 1889.

A New Mineral.—M. Des Cloizeau.—The author exhibited some crystals of a native platinum arsenide received from Mr. Wells, of Newhaven, Connecticut. This mineral contains 40·9 per cent of arsenic and 52·5 of platinum, along with antimony, rhodium, stannic acid, and traces of iron and palladium.

On the Oxidability and the Cleansing of Tin.—Leo Vignon.—The author's researches relate to the industrial processes of tinning iron and of soldering with tin. He has shown formerly that mixtures of metallic tin and stannous oxide, if heated in contact with air, do not melt, but burn. Such tin, however, may be made fusible by the addition of the substances which have been empirically used in tinning and soldering, such as zinc chloride, ammonium chloride, resin, borax, and caustic alkalies. Tin becomes oxidised rapidly both in moist and in dry air.

New Proximate Principle in the Ergot of Rye.—C. Tanret.—The substance in question is named ergosterine, and has the composition $C_{52}H_{40}O_2$. It is slowly oxidised on exposure to the air, becoming coloured and odoriferous. It is not attacked by strong boiling alkaline solutions. Like cholesterine it is a monoatomic alcohol. With nitric acid or hydrochloric acid and ferric chloride it gives the same reactions as cholesterine. But it dissolves completely in sulphuric acid, and chloroform, if shaken up with the mixture, remains colourless.

The Heptine of Perseite.—M. Maquenne.—This heptine is a non-saturated cyclic carbide, a kind of incomplete hydride, comparable, in its molecular structure, with the terpenes.

Zeitschrift für Physikalische Chemie, Stoechiometrie, und Verwandtschaftslehre. Vol. ii., Part 11.

The Connection between the Molecular Properties of Inorganic Compounds and their Action upon Animated Matter.—J. Blake.—The author expresses his conviction that animated matter may serve as an important reagent for the physico-chemical properties of bodies, and these properties bear an important relation to a branch of science with which they have not yet been connected. The first fact which the author establishes is that the reactions produced upon living animals depend upon the electro-positive constituent of a salt, and are little affected by the nature of the acid radicle. If introduced directly into the blood the sulphates, nitrates, chlorides, acetates, arseniates, and phosphates of one and the same base exert all the same biological action. This rule has been found to hold good with more than forty elements, the only exceptions being potassium and ammonium, to which the author refers below, and it extends not merely to compounds of the more electro-positive elements, but even to the halogens. Dr. Blake has previously shown that the atomic weight of an element is an important factor in its biological action, and has an influence upon its general character, which depends on the isomorphous relations of the substances. It was found that in bodies of one and the same isomorphous group the intensity of the action is proportional to the atomic weight. In other words, the higher the atomic weight of an element the less of it need be present to bring on the symptoms indicative of the peculiar isomorphous group to which it belongs. This rule holds good only for the electro-positive elements. In the non-metals the biological action is, indeed, determined by their isomorphous relations, but there appears no connection between the atomic weight and the intensity of their action. Another fact is the connection between the molecular constitution of inorganic substances and their effects upon living matter, the valence of an element being a factor in its biological action. It is not the general character or the intensity of the biological action, but, so to say, its *extent* which is affected by the valence of the element. As the valence rises so does the number of the organs upon which the organic substances act. Mono-valent elements are known by their effects upon the pulmonary capillaries. Even if injected into the arteries they exert no definite action upon the nerve-centres, and they kill by the changes which they occasion in the lungs. The di-valent elements, both of the Mg and the Ba group act, by destroying the excitability of the muscles of the heart. They have an influence also upon certain peripheric nerves, the Mg group upon those of the intestines and the Ba group upon those of the voluntary muscles. The biological action of the tri- and tetra-valent elements is much more extensive, as they affect the functions of all the more important nerve-centres. It is evident that the phenomena in question are not related to ordinary

chemical reactions. The fact that we have in an isomorphous group of salts a series of reagents, each of which produces analogous biological effects, and that the higher the position of an element in these series the smaller is the quantity needed to produce an equally strong effect, distinguishes these effects clearly from those of an ordinary chemical transposition. In 1885 the author pronounced these reactions as catalytic, and in a recent memoir Professor Ostwald declared that the reactions taking place in living matter might be generally thus regarded. Dr. Blake is not certain that a relation can be demonstrated between these catalytic phenomena and the isomorphous characters of the elements, but we have certain indications that atomic weight and valency are factors in catalytical reactions. As to the influence of isomorphism, it seems to be the main determining factor in these biological reactions. Among all the substances examined two exceptions only have occurred, the salts of potassium and ammonium. The influence of the isomorphous relations of elements in its action upon living matter appears most conspicuous when they form the transition members between two isomorphous groups. They produce biological effects which are analogous to those occasioned by the elements of both the adjacent groups. The salts just mentioned, which have isomorphous relations both with the mono-valent metals and also with the Ba group, are distinguished by their action upon the pulmonary capillaries, like those of the Na group, whilst at the same time they bring on the most characteristic reaction of the salts of the Ba group—they delay the contraction of the voluntary muscles for several minutes after death. If one and the same element forms compounds belonging to two isomorphous groups the action of such salts is by no means mutually identical. Such are the connections manifested between the action of inorganic compounds upon living matter, and some of their most important molecular properties. From the experiments of other observers it seems as if a similar connection between molecular constitution and biological effects exists in the hydrocarbons. Dujardin-Beaumetz has shown that in homologous series of alcohols the poisonous properties increase with the molecular weight, and Schmiedeberg finds that the biological action of the esters does not depend on their electro-negative constituent. The author refers to certain researches of Gerhard Krüss, which we purpose shortly to notice, and expresses the opinion that as we have in living matter a substance in a condition of perpetual transformation, and that the result of such transformations is the production and modification of vibrations in the nervous tissue which are communicated by the nerves to the various organs, we might expect, *à priori*, that by means of the molecular vibration of our reagents the reactions occurring in the nervous tissue will undergo a direct or indirect modification. Whilst these considerations open up a new point of view for the investigation of biological phenomena, the author considers the connection between chemical constitution and biological action to be so clearly manifested that living matter forms a valuable reagent in the examination of the molecular constitution of bodies.

The Dissociation Theory of the Electrolytes.—J. H. van't Hoff and L. Th. Reicher.—The authors extended Avogadro's law to solutions if only osmotic pressure takes the place of the pressure of tension in the case of gas; or, in other words, the osmotic pressure of all dilute solutions and the pressure of tension of all dilute gases have the same value at the same molecular concentration and the same temperature. But at the same time they admitted that the aqueous solutions of most salts, acids, and bases seemed to be different, their osmotic pressure being often considerably greater than it should be expected. Arrhenius soon after sought to explain this anomaly, showing that in the substances concerned the anomalous behaviour in aqueous solutions is due to a partial splitting up, which is fully manifested in electrolysis. The authors are now able to confirm the explanation of Arrhenius.

The Dissociation of Carbonic Acid.—H. Le Chatelier.—After giving a sketch of the history of researches on this subject, that author informs us that according to the experiments of M. Mallard and himself the dissociation of carbonic acid only begins to be perceptible above 2000°. At this temperature and at a pressure of six atmospheres it is less than 0·05. At 3300° it is considerably advanced. The results obtained do not agree with the general opinion that at a sufficiently elevated temperature all substances would undergo a complete dissociation. There are cases in which the existence of a maximum of dissociation has been observed. Such are the experiments of Troost and Hautefeuille on the dissociation of silicon chloride, and those of Ditte on hydrogen selenide.

Rapidity of the Reaction in the Oxidation of Tartaric Acid.—Jean Krutwig.—This paper does not admit of useful abridgment.

Electro-chemical Studies. Sixth Memoir: Relations between the Composition of the Ions and their Rapidity of Translation.—W. Ostwald.—Isomeric ions are translated with an equal rapidity. The rapidity of translation decreases with an increase of the number of the atoms contained in the ion. The nature of the component elements has an influence on the rapidity of translation, which, however, is distinct only in ions of simple composition. If the number of the atoms in an ion is more than about twelve the rapidity of translation depends almost exclusively on this number. The totality of these results justifies the conclusion that a sufficiently approximate determination of the maximum conductivity of an acid can be arrived at from its composition alone.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Plaster of Paris.—Where can I obtain particulars as to the various details of the manufacture of the above?—GYPSUM.

MEETINGS FOR THE WEEK

MONDAY, 4th.—Medical, 8.30.
—— Society of Chemical Industry, 8. "Some Industrial Applications of Oxygen," by Dr. T. L. Thorne. "Note on Improved Laboratory Apparatus," by Dr. T. W. Leathes.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 5th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
WEDNESDAY, 6th.—Society of Arts, 8.
—— Geological, 8.
THURSDAY, 7th.—Royal, 4.30.
—— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
—— Royal Society Club, 6 30.
—— Chemical, 8. "Researches on the Constitution of Azo- and Diazo-Derivatives—Part V.," by R. Meldola, F.R.S., and G. T. Morgan. "Résumé of Researches on the Laws of Substitution in the Naphthalene Series," by H. E. Armstrong. "The Action of Nitric Acid on Anthracene," by A. G. Perkin. "Note on Methyl Fluoride," by N. Collie.
FRIDAY, 8th.—Quekett Club.
—— Astronomical, 3. (Anniversary).
—— Royal Institution, 9. "Electrostatic Measurement," by Sir William Thomson, F.R.S.
SATURDAY, 9th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.
—— Physical, 3. Annual General Meeting. "On Physico-Geometrical Models," by Prof. A. S. Herschel.

THE LONDON GEOLOGICAL FIELD-CLASS LECTURES on the "THAMES VALLEY," by PROFESSOR H. G. SEELEY, F.R.S., in Holborn Town Hall, Gray's-Inn Road, every Wednesday Evening from February 6th to the 27th, at 8 o'clock. Tickets, 5s. each for the Course. may be had from W. Wesley and Son, 28, Essex Street, Strand, W.C.

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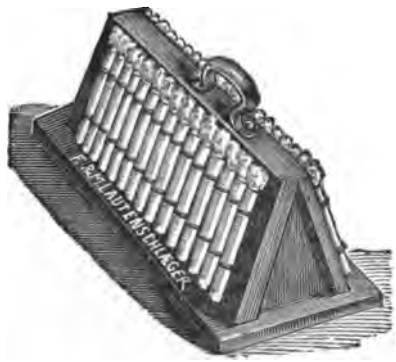

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THE CHEMICAL NEWS.

VOL. LIX. No. 1524.

THE DECOMPOSITION OF POTASSIUM CHLORATE IN CONTACT WITH METALLIC OXIDES.

By Dr. W. R. HODGKINSON and F. K. S. LOWNDES.

In the CHEMICAL NEWS, vol. lviii., p. 309, we mentioned a number of qualitative reactions bearing on the function of MnO_2 and other oxides in the decomposition of potassium chlorate by heat. Our work on this subject is now so far advanced that we are enabled to give a more rational explanation of this peculiar action supported by analyses.

It is usually supposed that when $KClO_3$ and MnO_2 are heated together, the MnO_2 remains as such in the vessel together with KCl. In only exceptional cases does this appear to be the case. The manganese is to a greater or less extent in the form of lower oxides. Only when the mixture has been heated until the whole of the oxygen is driven off and a gentle heat maintained for some time, is the manganese completely re-oxidised.

In one case only out of a number, 14 or 15, were we able by continuous heating to obtain MnO_2. In this series of experiments a weighed quantity of pure $KClO_3$ was heated with a weighed amount of MnO_2 in a cleaned weighed test-tube; the residue remaining in the tube was weighed after cooling.

0·2779 $KClO_3$ and 0·0328 MnO_2 gave a residue of 0·1104, consisting of KCl and oxide of manganese. The theoretical quantity corresponding to KCl and MnO_2 being 0·1110, gave a difference of only 0·0006, which could be accounted for by errors of experiment.

Altogether eight experiments on this point were made; they are numbered consecutively.

In experiments 1 and 2 (Table) the loss of oxygen appears to correspond with that contained in the chlorate only. In 6 and 7 the mixture was at first heated to such a temperature that only part of the oxygen was given off; the tube was cooled and weighed, and again heated until the whole of the oxygen was evolved. In 8, after driving off all the oxygen and weighing, a fresh portion of $KClO_3$ was added, and the tube again heated. After the first heating the loss of oxygen was nearly theoretical: experiment, 0·4074; theory, 0·4088. 0·1672 grms. of $KClO_3$ was added containing 0·0655 grm. O. After treating the second time the loss was not so great as it should have been theoretically, it being 0·0638 grm.

In all these experiments it was noticed that just before the last traces of oxygen were being driven off the mass of solidified substance in the tube began to glow as if oxidation was taking place, which passed, more or less, completely throughout the whole mass. These experiments appear to point to the conclusion that the manganese is alternately *reduced* and re-oxidised by the $KClO_3$, but only in exceptional cases is the re-oxidation complete. This reduction in a strongly oxidising atmosphere is probably due to the atomic attraction of the oxygen; in both the $KClO_3$ and MnO_2 they pull at each other, and the force of attraction combined with the decomposing effect of the temperature is sufficient to break up both compounds.

In support of this idea may be mentioned the facts that silver oxide is reduced to the metallic state by just fused $KClO_3$, and PbO_2 is reduced to Pb_3O_4.

The manganese oxide is physically altered, and in nearly all cases we find that a trace of manganate is formed, enough in fact to give a very distinct pink colour to the mass, especially when the chlorate was very largely in excess, and not heated for any length of time. What struck us as very strange, however, was the fact that when this was heated with water the pink colour of the solution was very evanescent, disappearing almost at once. We found the explanation of this peculiarity when, upon mixing with a solution of permanganate, finely divided MnO_2, the colour of the former was completely taken away, and no manganese salt went into solution. It was reduced apparently to MnO_2 and potash. This appears to account for the formation of a manganate apparently never having been particularly noticed. Having found that there was a deficiency in the weight of residue, we next endeavoured to prove that the difference was indeed due to the reduction of MnO_2. In these experiments a weighed quantity of MnO_2 was mixed with an excess of $KClO_3$, and the whole heated to drive off all the O; as soon as the tube was cooled enough water was put in and boiled, the insoluble matter filtered off and well washed on a weighed filter-paper. After drying the whole was again weighed.

	MnO_2 taken.	Residue after filtering, &c. (MnO_2).
Expt. I.	0·0647	0·0643
„ II.	0·0600	0·0618

It appears from these experiments that the manganese is in the state of dioxide, and that these experiments contradict the previous ones.

This, however, is probably not the case, as the water used for washing seems to be decomposed by the lower oxides formed, and the oxygen re-oxidising them to MnO_2. In fact, a considerable quantity of some gas is always given off as soon as the water is added. This we take to be hydrogen from the decomposed water, but have not yet been able to collect in quantity for proof.

As is partly known, a large number of other oxides enable potassium chlorate to give its oxygen up at a lower temperature. The action on the chlorate depends, however, upon the nature of the oxide. Some, in addition, cause the evolution of quantities of chlorine, but only those oxides capable of giving salts with the potassium oxide do this to any extent.

Some basic oxides act on the MnO_2, but do not give off Cl; others, such as SiO_2, TiO_2, are quite inactive, although they are to a certain extent acid-forming oxides, but only at a very high temperature. A number of analyses have been made by us to ascertain the relation between the amount of oxide used and the quantity of chlorine liberated. The following oxides were used:—$(UO_2)(OH)_2+OH_2$, U_2O_5, and V_2O_5. In these experiments 3 grms. pure $KClO_3$ were mixed in a small distilling bulb with a weighed quantity of the oxide under examination, and the gases obtained by heating sent

No	$KClO_3$.	MnO_2.	Theory O for MnO_2.	Theory O for $KClO_3$.	Total O theoretical.	Loss of O found.	Difference between theory and experiment.
1.	0·4235	0·0990	0·0091	0·1649	0·1740	0·1669	0·0071
2.	0·7109	0·1068	0·0098	0·2768	0·2866	0·2762	0·0104
3.	0·2779	0·0328	0·0030	0·1800	0·1110	0·1104	0·0006
4.	1·0161	0·0502	0·0046	0·3980	0·4026	0·3900	0·0126
5.	0·9155	0·0979	0·0101	0·3553	0·3654	0·3629	0·0025
6.	0·3383	0·0698	0·0064	0·1312	0·1378	0·1322	0·0056
7.	0·7434	0·1859	0·0170	0·2910	0·3080	0·2935	0·0145
8.	1·1930	0·1440	0·0104	0·4639	0·4733	0·4712	0·0021

through the side tube into a solution of KI; the amount of liberated I was then determined by standard thiosulphate solution, and calculated into chlorine.

I. *Yellow Hydrated Oxide of Uranium*, $(UO_2)_2(OH)_2+H_2O$.

Equation for reaction—

$$2KClO_3+2(UO_2)(OH)_2+2H_2O=2H_2O+K_2U_2O_7+Cl_2+O_4.$$

(3 grms. $KClO_3$ used).

a. 0·0698 uranium oxide liberated 0·00740 Cl
Theoretical amount of Cl = 0·00760 ,,

β. 0·1127 uranium oxide liberated 0·01285 Cl
Theoretical amount of Cl = 0·01227 ,,

γ. 0·1292 uranium oxide liberated 0·01443 Cl
Theoretical amount of Cl = 0·01407 ,,

II. *Red Oxide of Vanadium*, V_2O_5.

(3 grms. chlorate used).

a. 0·0202 uranium oxide liberated 0·00888 Cl
Theoretical amount of Cl = 0·009 ,,

β. 0·0304 V_2O_5 gave 0·010545 Cl
Theoretical amount of Cl = 0·0109 ,,

γ. 0·0259 V_2O_5 gave 0·00934 Cl
Theoretical amount of Cl = 0·00925 ,,

Uranium pentoxide, black or dark green, scarcely acts upon $KClO_3$, and the chlorine evolved is not a proportionate amount.

a. 0·2295 U_2O_5 gave 0·00226 Cl
Theoretical amount of Cl = 0·0284 ,,

β. 0·21615 U_2O_5 gave 0·001319 Cl
Theoretical amount of Cl = 0·0269 ,,

A number of salts, especially those of ammonia, are very active in decomposing $KClO_3$, and are of course at the same time decomposed by it. NH_4Cl, when heated with $KClO_3$, evolves an amount of chlorine equal to that contained in itself, but the nitrogen apparently is not oxidised.

0·1909 NH_4Cl evolved 0·15995 Cl
Theoretical amount of Cl = 0·15600 ,,

$$6NH_4Cl+4KClO_3=12H_2O+4KCl+3Cl_2.$$

With some other ammonium salts we are not so sure that some oxide of nitrogen or nitrogen oxychloride is not formed.

Tungstic and molybdic oxides are so eminently acid that we did not think it worth while to do any quantitative experiments with them. They no doubt expel all the chlorine. Ordinary cerium oxide, Ce_2O_3, containing La and Di, does not appreciably act on melted chlorate.

Royal Military Academy,
Woolwich.

SOLUTION FOR DEPOSITING METALLIC COBALT.

By H. N. WARREN, Research Analyst.

The cobalt salt, preferably the chloride, is dissolved in a sufficiency of water at a temperature of about 100° F., and a concentrated solution of Rochelle salt added until tha bulky precipitate at first formed has almost entirely re-dissolved. The solution, filtered if necessary from any insoluble precipitate, is electrolysed with the utmost ease by connecting the article intended to receive the deposit with the negative electrode of any single cell battery. The opposite, or positive electrode, which is composed of a zinc rod immersed in a saturated solution of either ammonium chloride or common salt, and protected from contaminating the cobalt solution by the intervention of a porous pot surrounding the zinc. On completing the circuit the cobalt is immediately deposited in a uniform layer, and at the same time presenting a perfectly bright surface. On substituting nickel chloride in place of the cobalt salt metallic nickel may be similarly deposited. It has also been observed on several occasions that by employing a solution holding both nickel and cobalt salts in solution that the deposit thus obtained was considerably darker as regards shade, and also more durable than when cobalt alone was used, the deposit thus produced consisting of both nickel and cobalt in almost exact proportions. Zinc and several other metals may be also deposited by the same means.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

RESEARCHES ON COBALT AND NICKEL.

By GERHARD KRUSS and F. W. SCHMIDT.

The authors, who were engaged in a re-determination of the atomic weights of these metals, did not succeed in obtaining either the values of Zimmermann (Co=58·74, Ni=58·56), nor the almost respectively identical figures of Russell and Winkler. It was found impossible to precipitate from a neutral solution of gold chloride an equivalent quantity of absolutely pure gold by means of nickel or cobalt. In consequence of polarisation traces of cobalt and nickel were re-precipitated from the solutions of cobalt or nickel which had been formed and remained in admixture with the gold. In order to determine the quantities of metal which had entered into reaction, the precipitated gold, after being perfectly washed, dried, and ignited, was weighed. It was then re-dissolved in aqua regia, and, after expelling the excess of acid, the gold in solution was precipitated with sulphurous acid. The weight of gold thus obtained was smaller than the former weight, and the difference of both values was deducted from the weight of the cobalt or nickel originally employed.

Despite these precautions the results were so fluctuating that their differences could not be due to ordinary analytical errors. It became therefore necessary to examine the solutions and washing-waters. On washing the gold thrown down by means of sulphurous acid from a solution of the metal precipitated by cobalt, the authors observed the following phenomenon:—The red colour of the filtrate, owing to cobalt chloride, became by degrees paler, and changed then to a faint greenish shade, barely perceptible. This portion of the washings was therefore collected separately, and evaporated down in a platinum capsule. After ignition it left a slight residue, which dissolved with a fine green colour in hot and strong hydrochloric acid: on cooling the liquid became almost completely colourless.

Analogous phenomena were observed in determining the atomic weight of nickel. Here also, by concentrating the last washings and re-dissolving in hydrochloric acid, there was obtained the solution of a chloride in which neither nickel chloride nor any other known compound could be detected. The quantity of this chloride being very small, the authors instituted a number of experiments, and finally obtained a pure oxide by utilising the observation that the oxide in question was soluble in melting alkali, in which nickel and cobalt oxides are insoluble. These experiments will shortly be described in full.

The acid solution of the chloride is not precipitated by sulphuretted hydrogen, but ammonium sulphide throws down a blackish sulphide from the neutral solution. Ammonia precipitates the neutral solution of the chloride in voluminous white flakes, resembling zinc or aluminium hydroxide. An excess of ammonia does not re-dissolve the precipitate.

Semi-normal potassa also throws down a snow-white hydroxide, which cannot be re-dissolved, even by a great excess of the precipitant. This excludes alumina, of which not the slightest trace could be detected in the oxide in question. If moistened with a solution of cobalt and ignited it yielded not Thénard's blue, but took a faint light brown colour. If strongly ignited for a long time with the blast the oxide yielded a fine white powder, which dissolved readily and completely in cold hydrochloric acid at 27 per cent of strength. The strongly acid solution of the chloride displayed its peculiar greenish yellow colour. When perfectly dry and free from excess of acid the chloride is white, and forms a colourless solution in water. If the white chloride is treated with the vapour of hydrochloric acid it turns green and yields a green solution in water.

In a current of hydrogen the oxide does not behave like the nickel and cobalt oxides, since even at the strongest heat it undergoes no loss of weight. But the metal corresponding to the white oxide can be obtained by the electrolysis of an aqueous solution of the chloride. The chloride can likewise be reduced at a red heat in a current of hydrogen if it has been previously dried in a current of carbonic acid. The metal is black, or in thin layers a brownish black, readily soluble in acids if it has been obtained electrolytically in the cold; but it is much less readily soluble if it has been heated to redness or whiteness in a current of hydrogen.—*Berichte der Deutschen Chemischen Gesellschaft*, Vol. xxi., No. 1, p. 11.

INCOMPLETENESS OF COMBUSTION IN GASEOUS EXPLOSIONS.*

By Prof. HAROLD B. DIXON, F.R.S., and H. W. SMITH, B.Sc., Dalton Chemical Scholar, Owens College

In the course of an investigation in which we were engaged, on the rate of propagation of gaseous explosions, it was noticed that when a mixture of hydrogen and oxygen, in the proportions in which they combine to form water, was exploded, there remained an explosive residue in addition to the unavoidable slight excess of one or the other gas due to inaccuracy in mixing. The mixture was exploded in a leaden tube 100 m. long and 9 m.m. in diameter; after the explosion the tap at one end was opened, and air allowed to rush in. Air was then pumped in by a bellows, and the other tap was then opened. On applying a light to the out-rushing gases for the purpose of determining whether the hydrogen or the oxygen was in excess in the original mixture, the gas at first driven out proved to be rich in oxygen—supporting combustion vividly—and then the succeeding gas burnt with a series of sharp cracklings, and finally there was a flash down the tube.

From this it appeared that even in a mixture of hydrogen and oxygen, containing a slight excess of oxygen, the hydrogen was not completely burnt. If the mixture had contained an excess of hydrogen it might have been reasonably supposed that the explosive residue was made up of the excess of hydrogen and the air admitted after the explosion. This explanation could not be admitted in the present instance, as the mixture contained an excess of oxygen. A similar phenomenon was observed when a slight excess of hydrogen was employed, and the residue was swept out of the tube by a stream of carbonic acid gas.

Led by these experiments we began the investigation, an account of which is given in the following paper. Our object was to determine the conditions affecting the amount of this explosive residue, especially the influence of the surface exposed to the exploding gases.

Mixtures containing slight excess, first of hydrogen and second of oxygen, were employed, and in all cases the residues were collected and analysed. The first series of experiments was made with the tube mentioned above, which was 100 m. long and 9 m.m. in diameter, the surface exposed to the gases being about 29,000 sq. c.m. After each explosion CO_2 was admitted at one end of the tube until the pressure was equal to that of the atmosphere, and then one litre was driven out and collected over caustic soda solution at the other end of the tube. It was found that the first litre driven out contained practically all the gas left after explosion. The amount of residue varied from 100 to 250 c.c., according to the accuracy of the mixture and the amount of nitrogen as impurity in the original gas, and of air in the CO_2. We give below the mean results of analysis of a considerable number of residues; those given under A resulting from a mixture containing an excess of hydrogen, whilst in those given under B and C the original gas contained oxygen in excess.

I.

Explosions of Hydrogen and Oxygen.

(Capacity of tube, 8100 c.c.; diameter, 9 m.m.; internal surface, 29,000 sq. c.m.).

Mean composition of residue—

Average residue.		A.	B	C.
A—150 c.c.	H_2	54·3	29·5	20·5
B—160 ,,	CO		5·1	5·8
C—220 ,,	O_2	19·4	38·1	32·7
	N_2	26·3	27·3	41·0
		100·0	100·0	100·0

Per cent of original detonating gas unburnt—

Maximum	1·08	0·92	1·07
Minimum	0·69		
Mean	0·88		

With regard to the calculation of the amount of unburnt detonating gas, a slightly different method is employed according as the original gas contains excess of oxygen or hydrogen. All the residues contain a certain percentage of nitrogen, part of which is due to inleakage of air, and to air in the CO_2, used for sweeping out the tube, whilst part exists as impurity in the original gas, being chiefly derived from the water in the gas-holder. It is, however, impossible to determine accurately how much is due to each cause. In calculating the percentage of unburnt detonating gas, a maximum and minimum are taken in following way:—Firstly, assume all the nitrogen was present in the original gas, and calculate all the oxygen as belonging to the unburnt residue. This gives a maximum value for the percentage unburnt. Secondly, assume that all the nitrogen got in (as air) after the explosion, and from the percentage of oxygen deduct the amount of oxygen corresponding to the nitrogen (as air). In this way we get a minimum value for the amount of unburnt detonating gas, and the true percentage must lie between these limits. If there is a sufficient excess of oxygen we get only one value for the unburnt residue, viz., 1½ times the residual hydrogen. It will be observed that each of the residues contains a small percentage of carbonic oxide. Part of this is probably due to the grease used for the taps, and part may be due to hydrocarbons derived from the zinc used in the preparation of the hydrogen (except in cases where electrolytic gas was used). The carbonic oxide being a combustible gas must be taken into account in calculating the residual detonating gas. When there is an excess of oxygen the carbonic oxide is liable to get burnt, and therefore should be considered as a portion of the detonating gas left unburnt. When there is a deficiency of oxygen the carbonic oxide may be classed with the excess of hydrogen left over, and whether it affects the amount of unburnt detonating gas depends upon the quantity of oxygen remaining.

* A Paper read before the Manchester Literary and Philosophical Society, Oct. 2nd, 1888.

To determine the influence of the amount of surface exposed to the gases, a tube 4 m.m. in diameter was next employed. The length was about 170 m., and the internal surface, 25,000 sq. c.m., the capacity being 2750 c.c. The method of procedure was the same as before. Under A in the following table is given the mean of several analyses of residues from mixtures containing an excess of hydrogen, and under B, the mean result from mixtures containing an excess of oxygen.

II.	A.	B.
H_2	46·1	38·6
CO	14·9	12·4
O_2	16·3	25·4
N_2	22·7	23·6
	100·0	100·0
Average residue	75 c.c.	82 c.c.

Per cent of original detonating gas unburnt—

Maximum . ..	1·34	2·27
Minimum.. ..	0·84	1·55
Mean	1·09	1·91

The per cent unburnt under A does differ much from that obtained with the wider tube. Under B we see a rather larger percentage. In the next tables are given the means of analyses of residues obtained with a tube 19 m.m. in diameter (III.), and lastly (IV.), with an iron bomb made out of an ordinary mercury bottle attached to a firing tube. In the latter there are only about 1600 sq. c.m. of surface exposed for a volume of 3075 c.c.; that is to say, a surface only $\frac{1}{15}$ as great as that exposed in the 4 m.m. tube, the capacities being, however, nearly equal. From the analyses it would appear that although the amount of surface exposed to the gases has some influence on the amount unburnt, the influence is not very great, and therefore it seems improbable that the incompleteness of combustion is due to the cooling action of the surface of the vessel.

III.		IV.
C = 14,000 c.c.		C = 3075 c.c.
d = 19 m.m.		d = 100 m.m.
S = 28,000 sq. c.m.		S = 1600 sq. c.m.
Average residue 235 c.c.		100 c.c.
Mean composition of residue—		
H_2	44·2	8·2
CO	18·0	1·2
O_2	22·7	31·1
N_2	15·1	59·5
	100·0	100·0
Per cent of detonating gas unburnt—		
Maximum ..	1·16	0·46
Minimum ..	0·86	
	1·01	

A number of experiments were made with a mixture of carbonic oxide and oxygen.

In the first series of experiments the 9 m.m. tube was employed, and in the second series, the iron bomb. The mean results are given below.

In this case, therefore, we have also about 1 per cent of the original detonating gas left unburnt. The surface here does not appear to have much influence, the percentages unburnt being almost the same, although the surface exposed to the gases was, with the tube, about $3\frac{1}{2}$ sq. c.m. for each 1 c.c. of gas burnt, against 0·5 sq. c.m. per 1 c.c. of gas burnt with the bomb.

The fact that the incompleteness of combustion is characteristic of the explosive wave, and is not observed in the ordinary combustion in a eudiometer, has an important bearing on the theory proposed by Berthelot to explain

Carbonic Oxide and Oxygen.

I.		II.
C = 8100 c.c.		C = 3075 c.c.
d = 9 m.m.		d = 100 m.m.
C = 29,000 sq. c.m.		S = 1600 sq. c.m.
Average residue 205 c.c.		55 c.c.
Mean composition of residue—		
CO	26·0	41·4
H_2	1·7	6·7
O_2	30·2	27·1
N_2	42·1	24·8
	100·0	100·0
Per cent unburnt—		
1·06	Maximum	1·17
	Minimum	1·01
	Mean	1·09

the mode of propagation of the explosive wave, and also seems to confirm the observation made by Mallard and Le Chatelier, that the rate of cooling in this method of combustion is much more rapid than in the ordinary combustion.

THE VOLUMETRIC COMPOSITION OF NITROGEN OXIDES AND OTHER GASEOUS COMPOUNDS.

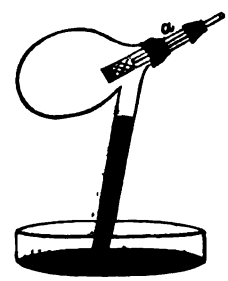
By P. HAWKRIDGE, B.A., late Scholar, Clare College, Cambridge.

CERTAIN text-book experiments have long been a puzzle to the Chemical Demonstrator, one in particular wherein it is proposed to determine the composition of certain gases by imprisoning them in a bent tube over mercury, the decomposition being affected by sodium, on the application of heat. The innocency of the pictorial representation is only equalled by the difficulty of its realisation. I think I am right in saying that few lecturers attempt these experiments, and yet they would be a welcome relief from the wearisome "Preparation and Properties" that are the bane of the chemical lecture room in so many cases.

The following description deals with practical methods for estimating the composition of several gases.

The chief trouble has been to get the metal into position without contact with the mercury. This difficulty is overcome as follows:—

Take a two-ounce retort. In the tubulure insert a closely fitting glass tube, A, and fasten it to the tubulure



by external indiarubber tubing. The interior end of tube A is closed by a plug of Italian asbestos rammed tight; next to it is the metal to be used, K, Na, Sn, &c., also closely packed to exclude as much air as possible; finally insert a glass rod, fitting closely into A, occupying the remainder of its length, and projecting beyond it. This is also fastened to the tube A by external indiarubber tubing. Fill the retort with mercury, place vertically

over the mercurial trough, pass up the gas, N_2O, H_2S, &c. Close the end of the neck by the finger, cork, or cushion, and push the glass rod ; the asbestos plug and metal fall into the bulb of the retort. Ligature all joints with copper wire, unclose the end of the neck, mark the height of the mercury, and effect the decomposition by heating the metal in the bulb.

As above described, the apparatus is only suitable for gases which, like N_2O and H_2S, have little or no action on the metals in the cold, and where no change of volume results. However, the system of rod, tube, and asbestos plug may be fixed on to the end of a bent tube, placed as in the text-book experiment; but, of course, the end must in that case be left open for the purpose. In this case the bent tube simply replaces the retort, and the experiment now becomes moderately well adapted for cases where the volume does not remain the same, as in the case of nitric oxide.

The method is inexpensive and efficacious.

I take this opportunity to point out that the retort, placed vertically as indicated in the above experiment, is a very good substitute for the much more expensive apparatus usually employed for demonstrating the composition of carbonic and sulphurous anhydrides. A little ingenuity will show how it should be used.

Schools of Science and Art,
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ON A NEW THORIUM MINERAL, AUERLITE.*

By W. E. HIDDEN and J. B. MACKINTOSH.

While one of us was about completing a contract for twenty-six tons of zircons, to supply a recent large demand for that mineral, several crystals of the mineral forming the subject of this paper were noticed in the very last shipments from the mine. As the quantity then found was insufficient for a complete chemical and physical examination, the locality was re-visited in July last, and for five weeks a systematic and laborious search for the mineral *in situ* was carried on. We had already proved it to be a hydrous mineral rich in thoria, with silica and, strangely, a very appreciable quantity of phosphoric acid. Our interest was centered upon its apparent anomalous composition, and a series of careful analyses were made by one of us as soon as the necessary material was procured. As the result of the search at the locality, not quite 100 grms. were found, and it became necessary to mine over 200 kilos. of zircons to get even this small amount.

It has thus far been found at only two places in Henderson County, North Carolina, namely, at the well-known Freeman mine, on Green River, and on the Price land, three miles south-westerly. At both places it occurs in disintegrated granitic and gneissic rocks intimately associated with crystals of zircons, and it is often seen implanted upon them—as a second or after-growth—in parallel position.

The colour on a fractured surface ranges in different crystals from a pale lemon-yellow through various shades of orange to a deep brown-red. The form is distinctly tetragonal, only the unit pyramid and prism being observed, and, excepting a tendency to a longer prismatic development, it is much like the common type of zircon found throughout the region. The faces being very rough and uneven, no constant angles could be obtained on any of the material, but they closely approximate to those of zircon.

Fragments of the mineral resemble some varieties of gummite and deweylite, but have a more waxy or rosin-like appearance. It is sub-translucent to opaque, and has a dull yellowish-white exterior. It is very brittle and easily crumbled. The hardness varies from 2·5 to 3, some crystals barely scratching cleavage surfaces of calcite. The specific gravity has a wide range, *i.e.*, from 4·422 to 4·766, the dark orange-red crystals having the highest density.*

The largest mass found measured 1 c.m. through the prism, and it was evidently only part of what had been a long crystal. The bulk of what we collected is in a very fragmentary condition, down to masses and broken crystals of 1 m.m. diameter.

Our analyses have given the following results :—

	1.	2.	3.	4.	5.
H_2O }	10·7	—	11·21	—	9·88
CO_2 }				—	1·00
SiO_2	—	9·25	7·64	8·25	
P_2O_5	—	—	7·46	7·59	
ThO_2	—	69·23	70·13		
Fe_2O_3	—	1·42	1·38		
CaO	—	—	0·49		
MgO	—	—	0·29		
Al_2O_3, &c.† ..	—	—	1·10		
			99·70		

If the amount of CO_2 in analysis No. 3 is assumed to be the same as it is in 5, and if we take the amount of H_2O as the difference between the loss on ignition and the CO_2, the ratio of hydrogen equivalents, of bases and acids (assuming the carbonates to be admixed impurity), is nearly 2 : 1 : 2. This gives the formula—

$$ThO_2, \left\{ \begin{matrix} SiO_2 \\ \frac{1}{2}P_2O_5 \end{matrix} \right\} 2H_2O,$$

or a thorite in which part of the silica is replaced by its equivalent in phosphoric acid, when $3SiO_2 = 1P_2O_5$. The ratio of silica to phosphoric acid is variable, and is approximately 1 : 1 in hydrogen equivalents; but the P_2O_5 tends to be in excess.

We have considered it possible that this mineral is a mixture of a hydrated thorium phosphate with a hydrated thorium silicate, in some respects analogous to the occurrence of zirconium silicate (zircon) in parallel position with yttrium phosphate (xenotime),‡ although there is nothing in the appearance to suggest this —the mineral seeming to be perfectly homogeneous, except on the exposed surfaces. It is more probable, however, that we have here an example of a partial replacement of silica by phosphoric acid, which fact has not yet, to our knowledge, been noticed in the literature of mineralogy ; unless we should so regard the small proportion of P_2O_5 (4·17) which Eakins§ observed in the xanthitane (altered titanite) from the same locality.

This occurrence of a thorium phosphate is the first instance of such a compound existing in nature, and seems to have a direct bearing upon the presence of thorium in monazite, and we believe that the idea that thorium is included in monazite as thorite—mechanically intermixed—should be modified in so much that the thoria should be considered as partially present as a phosphate, and the cerium earths partially present as silicates.

This mineral is readily soluble in hydrochloric acid, leaving a residue of gelatinous silica : after ignition it becomes insoluble. Thorium phosphate is generally regarded as a very insoluble compound, but the ready solubility of this mineral seems to disprove that opinion.

It is infusible, and upon strong ignition becomes dull brown, and, on cooling, orange again.

Thorite crystals having the form of zircon have been described by Zschau,‖ Nordenskiold,¶ and later, Brögger,**

* *American Journal of Science*, vol. xxxvi., Dec., 1888.

* Some of the crystals were much lighter in colour, softer, and of specific gravity from 3·7 to 3·8. These we propose to examine and report upon later.

† Including other oxides with traces of thoria.

‡ *American Journal of Science*, Nov. 1888, p. 380.

§ *Ibid.*, vol. xxxv., p. 418, May, 1888.

‖ *Ibid.*, II., xxvi., 359; see also "Dana's Syst. Min.," Ed. 1868, p. 413.

¶ *Geol. För. Förh.*, iii., 226, 1876; see also App. III., "Dana's Min.," p. 121.

** *Ibid.*, ix., 258, 1887.

have expressed the opinion that the mineral known as thorite is a pseudomorph after an original thorium silicate analogous to zircon in composition. This view is confirmed by the fact that this new mineral occurs intimately associated with and implanted upon perfectly unaltered zircon.

As this mineral was found while mining the very large quantity of zircons necessary to supply the demand caused by the invention of the system of incandescent gas-lighting of Dr. Carl Auer von Welsbach, we propose to name it *Auerlite* in his honour.

COMMITTEE* APPOINTED TO CONSIDER THE BEST METHOD OF ESTABLISHING INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

Objects.

It is proposed that the Committee shall co-operate with other similar committees in the more important iron-producing countries, in order to provide standard specimens of iron and steel, the chemical composition of which shall have been carefully determined. The specimens adopted as standards shall be entrusted to some recognised official authority, such as the Standards Department of the Board of Trade, and shall be used either for reference in the determination of the accuracy of any proposed method of analysis, or for controlling the results of analyses in any cases of importance which may from time to time arise.

Suggestions.

1. Professor J. W. Langley, of the University of Michigan, U.S.A., to be requested to superintend the production of the samples; that they be prepared and preserved in accordance with the directions to be furnished by the Committee, and that an equal portion of each sample be forwarded to the several Secretaries of the respective Committees in the United Kingdom, America, France, Germany, and Sweden.

2. The specimens which are eventually to be adopted as standards to be supplied to not more than seven representative chemists of repute in each of the countries above mentioned, who shall be requested to analyse the specimens by any method or methods they may prefer.

3. In the event of the analyses giving results, which in the opinion of the Committee may be regarded as sufficiently concordant, the means of the analytical results of each of the several constituents to be adopted as representing the composition of the standards. The report on the analytical results not to be issued before the various analysts, to whom the samples have been submitted, shall have had an opportunity of examining it. The standards shall hereafter be distinguished only by letters or numbers.

4. The attention of the Committee to be for the present confined to four samples of steel, selected as containing as nearly as possible 1·3, 0·8, 0·4, and 0·15 per cent of total carbon respectively. In addition to the determination of the amount of carbon present in each condition, the phosphorus, sulphur, silicon, manganese, and chromium also to be determined.

5. 150 kilos. of the samples selected for examination as standards to be prepared in all. This would give, after allowing sufficient for the required analyses, quite 5 kilos. of each standard for each of the five countries interested, allowing say 10 grms. for each applicant who may desire to use the standards, this would permit of 500 appeals to each of the four standards in each country, or at least 10,000 appeals in all.

6. The samples to be analysed in the United Kingdom by W. Jenkins, Dowlais; Edward Riley, London; J. E. Stead, Middlesbrough: The Royal School of Mines; G. S. Packer, of the Steel Company of Scotland, and two others.

7. The metal of which the samples are to be produced to be cast in small ingots, special care being taken to prevent any irregularity of composition. After the removal of the outer skin the metal to be cut by a blunt tool in the form of thin shavings, then crushed, sieved, and intimately mixed.

8. The samples thus prepared to be preserved in separate small quantities (say of 30 grms. each), which shall be hermetically sealed in glass tubes so as to prevent oxidation.

9. These preliminary arrangements of the Committee to be communicated to the leading technical journals.

* British Association for the Advancement of Science, Section B. Committee:—Prof. Roberts-Austen, F.R.S. (Chairman), Sir F. Abel, C.B., F.R.S., Prof. Langley, Edward Riley, G. J. Snelus, F.R.S., John Spiller, Prof. Tilden, F.R.S., and Thomas Turner (Secretary).

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

Methods for Determining Phosphoric Acid and Moisture.

(1). *Preparation of Sample.*—The sample should be well intermixed and properly prepared, so that separate protions shall accurately represent the substance under examination, without loss or gain of moisture.

(2). *Determination of Moisture.*—(*a*). In potash salts, nitrate of soda, and sulphate of ammonia heat 1 to 5 grms. at 130° C. till the weight is constant, and reckon water from the loss. (*b*). In all other other fertilisers heat 2 grms., or if the sample is too coarse to secure uniform lots of 2 grms. each, 5 grms., for five hours, at 100° in a steam bath.

(3). *Water-soluble Phosphoric Acid.*—Weigh out 2 grms. in a small beaker, wash by decantation four or five times with not more than from 10 to 15 c.c. of water, then rub it up in the beaker with a rubber-tipped pestle to a homogeneous paste, and then wash four or five times by decantation with from 10 to 15 c.c. of water. Transfer the residue to a 9 c.c., No. 589 Schleicher and Schüll filter, and wash with water until the filtrate measures not less than 250 c.c. Mix the washings. Take an aliquot (corresponding to ½ grm.) and determine phosphoric acid, as under total phosphoric acid.

(4). *Citrate-insoluble Phosphoric Acid.*—Wash the residue of the treatment with water into a 200 c.c. flask with 100 c.c. of strictly neutral ammonium citrate solution of 1·09 density, prepared as hereafter directed. Cork the flask securely and place it in a water-bath, the water of which stands at 65° C. (The water-bath should be of such a size that the introduction of the cold flask or flasks shall not cause a reduction of the temperature of the bath of more than 2° C.) Raising the temperature as rapidly as practicable to 65° C., which is subsequently maintained, digest with frequent shakings for thirty minutes from the instant of insertion, filter the warm solution quickly (best with filter-pump), and wash with water of ordinary temperature. Transfer the filter and its contents to a capsule, ignite until the organic matter is destroyed, treat with 10 to 15 c.c. of concentrated hydrochloric or nitric acid, digest over a low flame until the phosphate is dissolved, dilute to 200 c.c., mix, pass through a dry filter, take an aliquot and determine phosphoric acid as under total.

In case a determination of citrate-insoluble phosphoric acid is required in non-acidulated goods, it is to be made

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

by treating 2 grms. of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.), the residue insoluble in ammonium citrate is to be treated by one of the processes described below.

(5). *Total Phosphoric Acid.*—Weigh 2 grms. and treat by one of the following methods:—(1). Evaporation with 5 c.c. magnesium nitrate, ignition, and solution in acid. (2). Solution in 30 c.c. concentrated nitric acid with a small quantity of hydrochloric acid. (3). Add 30 c.c. concentrated hydrochloric acid, heat, and add cautiously and in small quantities at a time about 0·5 grm. of finely pulverised potassium chlorate.

Boil gently until all phosphates are dissolved and all organic matter destroyed; dilute to 200 c.c.; mix and pass through a dry filter; take 50 c.c. of filtrate; neutralise with ammonia (in case hydrochloric acid has been used as a solvent add about 15 grms. dry ammonium nitrate or its equivalent). To the hot solution for every decigrm. of P_2O_5 that is present, add 50 c.c. of molybdic solution. Digest at about 65° C. for one hour, filter, and wash with water or ammonium nitrate solution. (Test the filtrate by renewed digestion and addition of more molybdic solution). Dissolve the precipitate on the filter with ammonia and hot water and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralise with hydrochloric acid, cool, and add magnesia mixture from a burette; add slowly (one drop per second), stirring vigorously. After fifteen minutes add 30 c.c. of ammonia solution of density 0·95. Let stand several hours (two hours is usually enough). Filter, wash with dilute ammonia, ignite intensely for ten minutes, and weigh.

(6). Citrate-soluble phosphoric acid. The sum of the water-soluble and citric insoluble subtracted from the total gives the citrate-soluble.

Preparation of Reagents.

(1). *To Prepare Ammonium Citrate Solution.*—Mix 370 grms. of commercial citric acid with 1500 c.c. of water; nearly neutralise with crushed commercial carbonate of ammonia; heat to expel the carbonic acid; cool; add ammonia until exactly neutral (testing by saturated alcoholic solution of coralline) and bring to a volume of two litres. Test the gravity, which should be 1·09 at 20° C., before using.

(2). *To Prepare Molybdic Solution.*—Dissolve 100 grms. of molybdic acid in 400 grms. or 417 c.c. of ammonia of specific gravity 0·96, and pour the solution thus obtained into 1500 grms. or 1250 c.c. of nitric acid of specific gravity 1·20. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phospho-molybdate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(3). *To Prepare Ammonium Nitrate Solution.*—Dissolve 200 grms. of commercial ammonium nitrate in water and bring to a volume of two litres.

(4). *To Prepare Magnesia Mixture.*—Dissolve 22 grms. of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding excess of the latter. Add a little calcined magnesia in excess, and boil a few minutes to precipitate iron, alumina, and phosphoric acid; filter, add 280 grms. of ammonium chloride, 700 c.c. of ammonia of specific gravity 0·96, and water enough to make the volume of two litres. Instead of the solution of 22 grms. of calcined magnesia 110 grms. of crystallised magnesium chloride ($MgCl_2,6H_2O$) may be used.

(5). *Dilute Ammonia for Washing.*—One volume ammonia of specific gravity 0·96 mixed with three volumes of water, or usually one volume of concentrated ammonia with six volumes of water.

(6). *Nitrate of Magnesia.*—Dissolve 320 grms. of calcined magnesia in nitric acid, avoiding an excess of the latter; then add a little calcined magnesia in excess; boil; filter from excess of magnesia, ferric oxide, &c., and bring to volume of two litres.

Methods of Determining Potash.

Method of Lindo as Modified by Gladding.

(1). *Superphosphates.*—Boil 10 grms. of the fertiliser with 300 c.c. of water for ten minutes. Cool the solution; add a little oxalatate of ammonia, and then ammonia in slight excess, thus precipitating all phosphate and sulphate of lime, oxide of iron, and alumina, &c.; make up to 500 c.c., mix thoroughly and filter through a dry filter; take 50 c.c., corresponding to 1 grm., evaporate nearly to dryness, add 1 c.c. of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilisation of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water, plus a few drops of HCl; 5 c.c. of a solution of pure NaCl (containing 20 grms. NaCl to the litre) and an excess of platinum solution (4 c.c.) are now added. This solution is then evaparated to dryness in a small dish, the residue taken up with a little water, sufficient to dissolve it, and strong alcohol added. The precipitate is washed thoroughly with alcohol by decantation and on filter as usual. The washing should be continued even after the filtrate is colourless. 10 c.c. of the NH_4Cl solution, prepared as directed, are now run through the filter, or the washing may be performed in the dish. These 10 c.c. will contain the bulk of the impurities, and are thrown away. Fresh portions of 10 c.c. NH_4Cl are now run through the filter several times (five or six). The filter is then washed thoroughly with pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 grm. metallic platinum in every 10 c.c.

(2). *Muriates of Potash.*—In the analysis of these salts an aliquot portion, containing 0·500 grm., is evaporated with 10 c.c. platinum solution plus a few drops of HCl, and washed as before.

(3). *Sulphate of Potash, Kainite, &c.*—In the analysis of these salts an aliquot portion, containing 0·500 grm., is taken, 0·250 grm. of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c.c. platinum solution. In this case special care must be taken, in the washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colourless. 25 c.c. of the NH_4Cl solution are employed, instead of 10 c.c., and the 25 c.c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

To prepare the washing solution of NH_4Cl, place in a bottle 500 c.c. H_2O, 100 grms. of NH_4Cl; shake till dissolved. Now pulverise 5 or 10 grms. of K_2PtCl_6, put in the bottle, and shake at intervals for six or eight hours; let settle over night; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

Alternate Method.

In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, &c., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. Pulverise the fertiliser (200 or 300 grms.) in a mortar; take 10 grms., boil for ten minutes with 200 c.c. water, and after cooling, and without filtering, make up to 1000 c.c., and filter through dry paper. If the sample has 10 to 15 per cent K_2O (kainite), take 50 c.c. of the filtrate; if from 2 to 3 per cent K_2O (ordinary potash fertilisers), take 100 c.c. of the filtrate. In each case make the volume up to 150 c.c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner, add barium hydrate in slight excess. Heat, filter, and wash until precipitate is free from chlorides. Add to filtrate 1 c.c. strong ammonium hy-

drate, and then a saturated solution of ammonium carbonate until excess of barium is precipitated. Heat. Add now, in fine powder, 0·5 grm. pure oxalic acid or 0·75 grm. ammonium oxalate. Filter, wash free of chlorides, evaporate filtrate to dryness in a platinum dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a small filter, and washed with successive small portions of water until the filtrate amounts to 30 c.c. or more. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 5 to 10 c.c. of a solution of 10 grms. of platinic chloride in 100 c.c. of water. The mixture is now evaporated on the water-bath to a thick syrup, or further, as above treated with strong alcohol, washed by decantation, collected in a Gooch crucible or other form of filter, washed with strong alcohol, afterwards with 5 c.c. ether, dried for thirty minutes at 100° C., and weighed.

It is desirable, if there is an appearance of foreign matter in the double salt, that it should be washed, according to the previous method, with 10 c.c. of the half-concentrated solution of NH_4Cl, which has been saturated by shaking with K_2PtCl_6, as recommended by Gladding.

The use of the factor 0·3056 for converting K_2PtCl_6 to KCl and 0·19308 for converting to K_2O are continued.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 26, 1888.

Prof. FULLER, F.R.S., in the Chair.

THE thanks of the Society were tendered to Mr. Freeman for presenting to the Library a rare and interesting work —"Réflections sur la Puissance Motrice du feu et Sur les Machines propres a dévellopper cette puissance, Par S. Carnot, ancien élèvede L'Ecole Polytechnique.

Dr. S. P. THOMPSON read three notes on Polarised Light entitled respectively:—"*The Structure of Natural Diffraction Gratings of Quarts*;" "*Ahrens's Modification of Delezenne's Polariser*;" and "*The Use of Two Quarter Wave Plates in Combination with a Stationary Polariser.*"

Two microscope slides of iridescent quartz (prepared by the late Mr. Darker), which have recently come into possession of the author, exhibit remarkable peculiarities. Both act like diffraction gratings, one as if the rulings were about 12,000 and the other about 26,000 to the inch. On examining the specimens by the microscope it was found that the parts which exhibited the grating effect showed a spindle-like structure, and by micrometer measurements the dimensions of the spindle-shaped bodies were determined to be from 1-1000th to 1-3000th of an inch in diameter and 1-100th to 1-300th of an inch long. These were much too large to cause the effects noticed, but on closer examination it was found that the bodies were crossed at right angles by fine markings, the distances between which are in close accordance with those deduced from the spectra produced. As a probable cause of the phenomenon the author mentioned a recent paper by Prof. Judd "On the Production of a Lamellar Structure in Quartz by Pressure," and suggested the possibility of making diffraction gratings by such means.

Ahrens's modification of Delezenne's polariser consists of a total reflection prism combined with glass plates and black glass mirror arranged so that the polarised beam is parallel to the original one. The combination of plates and mirror is adopted so as to give enough light and still keep the polarisation sufficiently good. One or two plates laid over the mirror are found to give the best results.

The fact that a beam polarised by reflection is not coincident with the original beam renders it inconvenient, if not impossible, to rotate the polariser, and to overcome this defect the author has arranged two quarter wave plates, one of which may be rotated. The first plate circularly polarises the plane polarised beam, and the second (or rotating one) re-plane polarises it in any desired plane. Objects were shown on the screen to illustrate the degree of perfection attainable by using the new polariser in combination with the two quarter wave plates.

A "*Note on a Relation between Magnetisation and Speed in a Dynamo Machine*" was read by the same author.

In a note presented to the Society in June last it was shown that $\Sigma\rho.\Sigma R = 4\pi nCS$, where $\Sigma\rho$ and ΣR are the magnetic and electric resistances respectively, n = speed, and C and S the numbers of armature and field windings. By writing the equation in the form—

$$\frac{4\pi CS}{\Sigma R} = \frac{\Sigma\rho}{n}$$

it is seen that *when the electric resistance is maintained constant the magnetic resistance is proportional to speed.*

Prof. HERROUN read selections from a paper "*On the Divergence of Electromotive Forces from Thermochemical Data.*"

The fact that the electromotive forces of voltaic cells does not always coincide with calculated values has not hitherto received a satisfactory explanation, and this paper describes an experimental research bearing on the question. Several suggested explanations are given. In some cells the anticipated chemical change does not occur, and some metals become coated with oxide or sub-salts; others are affected by dissolved gases, and the hydration or solution of the salts formed may supplement or diminish the E.M.F. of a cell, as well as the absorption or evolution of sensible heat.

The question of absorption and evolution of heat is the one chiefly dealt with. If such actions do take place the total heat evolved by passing a definite current through the cell must depend on the direction of the current, and by enclosing the cell in a calorimeter the difference should be detected. The total heat developed by a current, C, in t seconds is—

$$\frac{C^2rt \mp \epsilon Ct}{J},$$

where r is the resistance of the cell and ϵ the divergence of the observed from the calculated E.M.F., the − or + sign depending on the direction of the current. In the case of mercury cells, which are usually said to give about half a volt excess E.M.F., the heat was found to be independent of the direction of the current. The heats of formation of mercury salts were then re-investigated, and the results showed that Julius Thomsen's numbers (the ones usually accepted) were greatly in excess of the true values. This accounts for the difference between the observed E.M.F.'s and those calculated from Thomsen's numbers. A copper silver-nitrate cell was tested in the calorimeter, and the reversible heat effect agreed closely with that deduced from the "thermo-voltaic constant," or divergence of observed from calculated E.M.F. Other experiments on tin, lead, nickel, and cadmium cells are described, and the chief conclusions arrived at are:—(1) The primary factor in determining the E.M.F. of a voltaic cell is the relative heat of formation of the anhydrous salts of the two metals employed. (2) That this E.M.F. may set up chemical changes of a different direction and character from those predicable from the heat of formation of the dissolved salts. (3) That the E.M.F. set up by (1) may be, and usually is,

supplemented by the energy due to the hydration or solution of the solid salts, and may have values which accord with the heat of formation of the dissolved salts. The absorption or evolution of sensible heat depends primarily on the attraction between the salts and water, combined with the heat of solution. Finally, the author states that the E.M.F. of a cell gives a more accurate measurement of chemical affinity than data derived from calorimetric observations.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, February 4, 1889.

Sir James Crichton Browne, M.D., F.R.S., Vice-President, in the Chair

The following were elected Members of the Royal Institution:—John Tomlinson Brunner, M.P., Augustus Stroh, Sir Charles Tennant, Bart., and John Tennant.

Sixteen candidates for Membership were proposed for election.

The special thanks of the Members were returned to Mr. William Anderson for his present of a portrait of Professor Mendeleeff.

The special thanks of the Members were returned for the following donation to the Fund for the Promotion of Experimental Research:—Professor Dewar, £50.

The presents received since the last meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

The Retrospect of Medicine: Being a Half-yearly Journal containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by James Braithwaite, M.D. Vol. xcviii., July—December, 1888. London: Simpkin and Marshall.

In this valuable miscellany we find mention of a reagent producing a peculiar colour-reaction in the urine of patients suffering from typhoid fever. Two solutions are necessary; the one, called A, consists of 1 part of pure hydrochloric acid, 20 parts of water, and saturating with sulphurous acid. Mixture B consists of 1 part sodium nitrite, and water 200 parts. The test solution is made by adding 1 part of B to 25 parts of A, when wanted for use. Equal parts of the urine and of the test solution are mixed in a test-tube. and strong ammonia is freely added to make the whole alkaline. In normal urine the addition of the ammonia merely deepens the colour or produces a light reddish tint, and the deposit of phosphates, after 12 to 24 hours, retains its ordinary grey colour. In typhoid urines there is produced, on the addition of the ammonia, an intense scarlet, carmine, reddish orange, or even purple. The phosphatic deposit is coloured green, violet, or greenish black.

A new anæsthetic, discovered by Lewin, is put forward under the name of erythrophlaeine. Some doubt appears to exist whether this compound—if it is a definite chemical individual—is the active principle of *Erythrophlaeine judiciale*, or an extract from the venom of *Naja Najé*, better known as the cobra. In the latter case great care will doubtless be required in its administration.

For the detection of the bacillus of tubercle, Mr. Fargan recommends a Leitz oil-immersion object-glass of one-twelfth inch focus as quite equal in its performance to the Zeiss of the same power, and at nearly one-fourth of the price.

We find here no reference to any progress in the study of the ptomaines and leucomaines, which compounds a medical contemporary stigmatises as the "great unwashed."

A Year Book of Pharmacy: Comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry, contributed to British and Foreign Journals from July 1st, 1887, to June 30th, 1888, with the Transactions of the British Pharmaceutical Conference at the Twenty-fifth Annual Meeting, held at Bath, September, 1888. London: J. and A. Churchill.

We are happy to perceive that the abstracts in this volume are much better classified than it was in the case of its predecessors a few years ago. We no longer find placed under the general head "pharmacy" notices of manufacturing processes for substances which are not used in the treatment of disease. Many of the abstracts here inserted will have been already seen by most of our readers, but they are here collected in a form very convenient for reference.

The address of the President of the Conference contains not a few passages worth remembrance. We note especially a saying quoted from Nasmyth, of Manchester—"Touch and handle, remembering that gloves, especially kid gloves, are non-conductors of knowledge." Rarely, if ever, have we seen the necessity of experimental training and the impotence of mere book-study and paper-philosophy put so happily.

Those persons who think that everything is managed better abroad than in Britain may look at the course imposed in Belgium alike upon medical men and pharmacists. It includes zoology, which may be useful, but logic and *proh pudor* rhetoric! As we in England are already overrun with rhetoricians, we hope that this act will never be forced upon our medical men and pharmacists.

Elementary Inorganic Chemistry: Theoretical and Practical. With a Course of Chemical Analysis, and a Series of Examples in Chemical Arithmetic. By A. Humboldt Sexton, F.R.S.E., F.I.C., F.C.S., London: Blackie and Son.

We do not see that the work before us differs in any striking manner from many other elementary manuals of chemistry. It embraces only a portion of the recognised simple bodies, with their respective compounds; phosphorus, iodine, fluorine, silicon, along with some of their less important congeners, being omitted, whilst of the metals a few only are noticed. The least satisfactory feature of the work is its decidedly examinational character. We had hoped that, in prospect of a change in the educational wind, the compilers of elementary treatises on the sciences would have ventured to turn over a new leaf. We are very sorry to say that Mr. Sexton has made no such attempt. As he informs us in his preface, he "has thought it advisable to keep the requirements of the syllabus of the Department before him in preparing his book." In other words, he tacitly acquiesces in the "sacrifice of education to examination."

Sell's Dictionary of the World's Press. 1889 Edition. London: Sell's Advertising Agency, 167 Fleet Street.

A work of 1452 pages, full of important, useful, and, with rare exceptions, accurate information, and published at the low price of two shillings, may be considered as a prodigy, even in these days of enterprise. But we have here more, much more than a mere enumeration of journals of all kinds, with their places of publication and times of appearance.

We find here a careful abstract of the law of libel brought down to the present date, and rendered as intelligible as the subject admits. There are comments

on the influence of the Press upon language and style—by no means exclusively favourable. There is a commercial geography of the Indian Empire, and an essay on South Africa as a field for emigration. We find reminiscences of "Printers' Land," that district of London bounded north by Holborn, south by the Thames, and extending from St. Paul's on the east to Waterloo Place on the west, and a quantity of miscellaneous information which must be seen to be fully appreciated.

The weakest side of the work is that which deals with the scientific Press, British and especially foreign. Improvements have, indeed, been effected in this department in comparison with last year's edition, but some of the best known scientific and technical journals are still conspicuous by their absence. This is a point to be regretted, and we trust the proprietor will, in future editions, see his way to bring this part of his great compilation up to the level of the rest.

CORRESPONDENCE.

NICKEL AND COBALT.

To the Editor of the Chemical News.

Sir,—I have read with great interest the results of Krüss's experiments, published in the Chemical News and *Berichte*, on cobalt and nickel. I do, however, *not agree* with Krüss that the atomic weights of these metals, as found by Zimmermann, are in accordance with the periodic system, viz., Co = 58·74 and Ni = 58·56. On the contrary, the atomic weight of cobalt ought to be smaller than that of nickel, *i.e.*, about 57, as its highest oxide is an acid, and that of nickel not, so that the following will be the order of the atomic weights in the periodic system:—

Mn	Fe	Co	Ni	Cu
55	56	57	58·5	63
Mn_2O_7	Fe_2O_6	CO_2O_4 ?		

The atomic weight 58·7 hitherto found for cobalt may be due to the admixture of an element with the atomic weight of 153 or 248, most probably the new element discovered by Krüss.—I am, &c.,

B. Brauner.

Bohemian University, Prague,
February 3, 1889.

SEXTON'S INORGANIC CHEMISTRY.

To the Editor of the Chemical News.

Sir,—I am much obliged to "A Benighted Teacher" for calling my attention to an error which has unaccountably crept into my little book. The sentences should read:—"The composition of the gas may be determined by the first of the methods described for nitrous oxide, potassium being used in place of sodium."

"Leaves half its own volume of N on decomposition with K."

Apologising for occupying your valuable space, I am, &c.,

A. Humboldt Sexton.

Determination of an Alloy of Lead and Tin.—After treating such alloy with nitric acid in order to convert the tin into insoluble stannic acid, it is necessary to neutralise the excess of nitric acid by adding a very dilute solution of sodium hydroxide until a slight precipitate of lead begins to appear. This precipitate is then re-dissolved by means of a few drops of acetic acid, and the analysis is conducted as above.—*Journ. de Pharm.*, Vol. xix., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 3, January 21, 1889.

On the Electric Conductivity of Melted Salts.—Lucien Poincaré.—The author concludes that the coefficients of variation are inversely as the densities of the corresponding salts.

On Inverted Sugar.—E. Jungfleisch and L. Grimbert.—The facts observed by the authors lead to the conclusions that powerful acids modify the rotatory power of levulose, increasing it more or less according to circumstances. The levulose of sugar inverted by the procedures in common use is not identical with crystalline levulose, of which it may be considered an alteration-product.

The Extraction of Sorbite.—C. Vincent and M. Delachanal.—Sorbite forms an acetal with benzoic aldehyd. This acetal, by reason of its insolubility in water, renders it possible to extract sorbite rapidly in a pure state, and to detect it in vegetable liquids.

The Dibenzoic Acetal of Sorbite.—J. Meunier.—This compound is represented by the formula $C_{20}H_{22}O_6$, and contains two mols. of aldehyd.

Bulletin de la Société Chimique de Paris. Vol. li., No. 1.

Preparation of Iodoform.—H. Suilliot and H. Raynaud.—The authors take a solution containing 50 parts potassium iodide, 6 parts acetone, and two parts sodium hydroxide in one or two litres of cold water. Into this they pour, drop by drop, and with constant stirring, a dilute solution of sodium hypochlorite. Iodoform is quickly produced and precipitated. Further additions of the hypochlorite are made until all the acetone or all the iodide has disappeared.

On Tin.—Leo Vignon.—Already noticed under *Comptes Rendus*.

Conversion of Terpilene into a Menthene.—G. Bouchardat and J. Lafont.—It results from these researches that natural menthol should be connected with the terpilene series. This menthol has, with tepilenol or terpilene monohydrate, relations of composition like those which connect allylic alcohol to propylic alcohol.

Identity of the Active Principle of the Strophantus Glabrus of the Gaboon with Ouabaine.—M. Arnaud.—Already noticed.

On Dioxethylic Acetone.—E. Grimaux and L. Lefèvre.—This compound, $C_7H_{14}O_3$, is a colourless liquid of an aromatic odour, which distils at 195°. Its specific density is 0·980 at 17·8°. Its vapour density is 4·95, the theoretic figure being 5·05. It is soluble in alcohol and ether, moderately soluble in water, and volatilises along with watery vapour. It reduces the cupro-potassic liquor energetically, and in heat it reduces ammoniacal silver nitrate, yielding a mirror. It restores the colour of magenta which has been decolourised by sulphurous acid. It represents a mixed function, which has no analogues, being at once an acetone and the ethyl-ether of a bi-primary glycol.

Syntheses of Hydropyridic Bases.—A. and Ch. Combes.—The reactions indicated allow of the formation the derivatives of any closed chain whatever containing a single atom of nitrogen, excepting the pyrrol derivatives.

Reclamation of Priority on the Subject of the Process of M. l'Abbé Godefroy for the Disinfection of Alcoholic Phlegms by Hydrogenation.—Laurent Naudin.

Reply to L. Naudin.—M. Godefroy.—Of this stale controversy no further notice can be taken than to protest against the abuse of the term "disinfection" by both contending parties.

Volumetric Determination of Sulphates. — H. Quantin.—The author dissolves in 200 c.c. of distilled water 19·48 grms. of neutral potassium sulphate and 50 to 100 c.c. of pure hydrochloric acid and pours in slowly, stirring to dissolve the precipitate formed, 24·35 grms. barium chloride previously dissolved. He makes up to 1 litre and filters. Of this solution 50 c.c. precipitate from 0·3 to 0·4 of sulphuric acid. The excess of alkaline chromate involves a deduction as correction in all the readings. This correction is ascertained by precipitating with ammonia, in a total volume equal to that in which the determination is effected, the same quantity of barium chromate as in the analysis itself. Taking afterwards an equal fraction of the filtrate, we add a ferrous solution until a complnte reduction is effected. The correction should be about 0·2 to 0·5 c.c. This correction may be determined once for all by precipitating in a flask marked at 1000 c.c. 100 c.c. of the solution with an excess of ammonia, and reducing with the ferrous liquid 100 c.c. of the filtrate mixed with 5 c.c. of pure sulphuric acid. The ferrous liquid is prepared by dissolving 20 grms. double iron and ammonium sulphate and 10 c.c. of pure sulphuric acid in 1 litre of water. The operation is conducted as follows :—1 grm. pure dry potassium sulphate is dissolved in 600 c.c. of water in a flask marked at 1 litre, 100 c.c. of the barium chromate are added and shaken up. When the liquid begins to grow clear it is supersaturated with ammonia, when the liquid becomes of a sulphur yellow. It is filtered, and 100 c.c. of the perfectly clear liquid are taken, and to them are added 5 c.c. of pure sulphuric acid. The solution of iron is dropped in from a burette holding 50 c.c. The liquid turns from red to olive-brown green, and at last bluish green. At this moment little drops of the liquid are taken up with a glass rod and placed upon drops of ferricyanide on a white slab, stopping as soon as there is a blue tint. The solution of ferricyanide must be fresh and so dilute as to appear colourless. The salt must not be used as a dry powder. The actual determination is performed in the same way. Chlorides and nitrates do not interfere; chlorates must not be present and phosphates must be previously eliminated. All such cases may be previously prepared as follows:—The organic matter, if any, is destroyed by projecting the matter in small portions into pure melting sodium nitrate. The mass is dissolved in boiling water, and precipitated with a slight excess of ammonia along with calcium chloride. Lastly there is added a little sodium carbonate and the liquid is filtered.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 1.

Researches on Rhodium.— E. Leidié.— Already noticed.

On the Solom (*Dialium nitidum*).—E. Heckel and Fr. Schlagdenhauffen.—A botanical paper.

On Anagyrine.—E. Hardy and N. Gallais.—Already noticed.

Volumetric Determination of Lead by means of Potassium Ferrocyanide.—M. Yvon.—The author's process is expeditious. It involves neither the separation of tin nor the washing of precipitates. It is founded upon the action of potassium ferrocyanide upon lead salts. The precipitation is complete in the absence of free nitric acid. Free nitric acid does not interfere. The end of the operation is indicated by means of spotting with ferric chloride. The use of heat presents no advantage. Three solutions are needed. 1. A normal lead solution made with 15·987 crystalline lead nitrate and water enough to make up 1000 grms. Each c.c. represents 1 centigrm. of metallic lead. 2. Semi-normal solution of potassium ferrocyanide made with 10·201 grms. of the crystalline salt, and water to make up 1000 grms. Each c.c. represents a centigrm. of lead. The solution of ferric chloride must be so dilute that a drop when deposited upon the porcelain plate is not perceptibly coloured. For titrating the ferrocyanide solution the author pours into a large test-glass 10 c c. of the normal lead solution, and drops in with a burette the ferrocyanide solution, stirring meanwhile with a glass rod. The precipitate deposits rapidly; but it is not necessary to wait until the liquid is clear. When nearly 10 c.c. of the ferrocyanide solution have been added a series of drops of the ferric solution is placed upon a white plate, and a drop of the mixture is applied to one of these with a glass rod. As soon as a blue colour appears the addition of the ferrocyanide is stopped, and the number of degrees consumed is noted. Ten more c.c. of the lead solution are then added, and ferrocyanide is again added until the blue colour appears anew. If the process has been properly managed the second number of degrees read off on the burette will be exactly double the first, and the standard of the ferrocyanide solution is thus found.

No. 2.

On Solom (*Dialium nitidum*).—MM. Heckel and Schlagdenhauffen.—A pharmaceutical paper continued from the previous number. It is interesting to note that this fruit contains free tartaric acid and potasssium bitartrate, unaccompanied as in the tamarind by citric and malic acids.

On the Homopterocarpine and Pterocarpine of Red Santal Wood.—MM. P. Cazeneuve and L. Hugounenq.—From the *Bulletin de la Société Chimique.*

MISCELLANEOUS.

Separation of Stannic Oxide from Tungstic Acid.—E. Donath and F. Müllner.—The ignited and weighed mixture of both bodies as resulting in the analysis of the alloys by decomposition with nitric acid is ground in an agate mortar with twice its bulk of zinc powder or zinc filings, and ignited for fifteen minutes in a covered crucible. The spongy mass is treated with dilute hydrochloric acid (1 part acid and 2 parts water) in a covered beaker until there is no further escape of hydrogen. When it is cold potassium chlorate is added until the tungstic oxide is oxidised to yellow tungstic acid, diluted with 1½ vols. of water, let stand for twenty-four hours. The tungstic acid is washed first with water containing nitric acid, and finally with a dilute solution of nitric acid, and weighed. The tin may be either determined as difference, or directly by precipitating the filtrate with sulphuretted hydrogen.—*Chem. Centralblatt.*

The Oxidation of Hydrogen Iodide by the Oxy-acids of the Halogens.—Oskar Burchard.—In this investigation the author shows that the oxidation of hydrogen iodide by the oxy-acids of the halogens is a regularly progressive movement, the course of which is essentially determined by the concentration of the solution employed. The time requisite for the oxidation of a given quantity of substance depends on concentration in the same manner as Landolt has shown it to be the case in the oxidation of sulphurous acid. Of all the three oxy-acids used the one which acts most energetically upon hydrogen iodide is iodic acid, whilst chloric acid is least disposed to undergo any transformation with hydrogen iodide. The course and the duration of all these processes of oxidation depends on concentration, and it is extremely retarded in mixtures where both the components diminish in equal proportion. The rapidity of the oxidation is greatly increased by an excess of either of the reacting acids, equal equivalents of either producing like effects.—*Zeitschrift für Physikalische Chemie, Stoechiometrie, und Verwandtschaftslehre*, Vol. ii., Part 11.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Plaster of Paris.—(Reply to "Gypsum").—Short account in Bloxam's "Chemistry" (Churchill, London). Longer account in the "British Encyclopædia" (Black, Edinburgh). May be consulted probably at the large Free Libraries.—G. A. KEYWORTH, Hastings.

MEETINGS FOR THE WEEK

MONDAY, 11th.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Wood Engraving," by W. J. Linton.
TUESDAY, 12th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 13th.—Society of Arts, 8. "Salt; its Production and Consumption at Home and Abroad," by P. L. Simmonds, F.L.S.
—— Microscopical, 8. (Anniversary).
—— Pharmaceutical, 8.
THURSDAY, 14th.—Royal, 4.30.
—— Royal Institution, 3. "The Metamorphoses of Minerals," by Prof. J. W. Judd.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
FRIDAY, 15th.—Royal Institution, 9. "Electrical Stress," by Prof. A. W. Rücker, F.R.S.
—— Society of Arts, 8. "The Ruby Mines of Burmah," by G. Skelton Streeter, F.R.G.S.
—— Geological, 1. (Anniversary).
SATURDAY, 16th.—Royal Institution, 3. "The Character of the Great Composers and the Characteristics of their Works," by Prof. E. Pauer.

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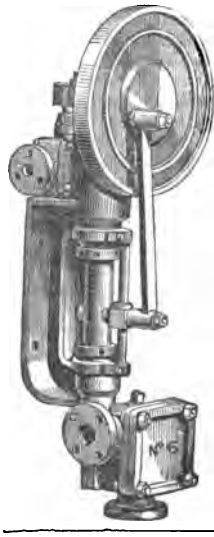

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THE CHEMICAL NEWS.

Vol. LIX. No. 1525.

A NEW SERIES OF ALUMINIUM COMPOUNDS.

Hitherto no substance has been known in which aluminium is present, not as aluminicum, but as aluminosum. A recent discovery has removed this anomaly. On fusing 58 parts of cryolite with 29½ parts of aluminium a double fluoride was obtained having the composition $2NaF,AlF_2$. The operation was first attempted in a crucible of gas-coke, atmospheric air being excluded during the entire process by means of a current of hydrogen. The product being found to be contaminated with aluminium carbide, the experiment was repeated in an iron crucible, polished internally and cased in platinum. The fusion was kept up for five hours, atmospheric air being excluded during the whole time, as before mentioned. The result was a homogeneous white compound, resembling cryolite in appearance, and having the exact composition stated above. It is to be hoped that other aluminous compounds will be obtained.

FERRO-MANGANESE WITH A LOW PERCENTAGE OF CARBON.

By SERGIUS KERN, M.E., St. Petersburg.

The late Mr. R. Hadfield produced a very useful metal, known as manganese steel. The less carbon there was in manganese steel the better it would be. Ferro-manganese containing 80 to 84 per cent of manganese contains also 5 to 6 per cent of carbon. How to eliminate the latter? Manganese is so easily oxidised that use of the refining furnace is out of question.

We desire to propose the use of the decarbonising process, used for the production of malleable castings from pig-iron.

The ferro-manganese, high in manganese, is cast from blast-furnaces into as thin as practically possible flat pigs. These pigs are heated in cast-iron boxes filled with a mixture of three-fourths of hematite powdered iron ore and one-fourth of lime, also in the form of powder.

We made several experiments on a small scale, which proved to be successful.

NOTES ON THE EXPLOSION OF A GAS CYLINDER.

By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

On January 28th a lamentable and fatal accident happened to Mr. Thomas Arthur Bewley by the explosion of a cylinder of compressed gas at the shipbuilding yard of Messrs. Bewley and Webb, East Wall, Dublin. The deceased gentleman established machinery for the compression of gases, and supplied the trade with compressed coal-gas and oxygen in wrought-iron cylinders. Owing to the uncertainty of the exact cause of the explosion a good deal of anxiety has been excited amongst the public.

The combustible gas, whether hydrogen or coal-gas, was stored in cylinders painted red and the oxygen in cylinders painted black. This rule was intended to be invariable. On December 27 Mr. Chancellor, of Sackville Street, sent an urgent request for a bottle of oxygen, but there being none of the black cylinders available, owing to the excess of business at Christmas-time, Mr. Chancellor was informed that he could be accommodated with oxygen in a red cylinder. This cylinder was returned on January 15. Afterwards, an application was made for a bottle of hydrogen and one of oxygen. It had been forgotten by the deceased that this bottle was charged with oxygen, and, being red, it was simply filled up and sent out as hydrogen.

It was attached to a lime-light apparatus, when the discovery was made that it contained mixed gases, for the indiarubber connecting tube was blown off as soon as the gas was ignited at the burner. It was placed on one side and labelled "mixed gases." Two days afterwards the bottle was sent back to Mr. Bewley and was placed on a table in the drawing office, where it remained until the fatal occurrence.

Instead of allowing the gas to blow off he tested a small quantity of the gas in a tube in presence of one of his foremen, who described the "spirt" with which it went off when a lighted match was applied to the mouth of the tube. The flame seen was a small blue one. He stated to the foreman that as the amount of inflammable gas was so small he intended to use the cylinder himself as an oxygen cylinder. As the pressure was higher than he required, a portion of the gas was allowed to pass into another black cylinder, which reduced its tension from 800 to 400 lbs. (the breaking strain of the bottle is well over 2000 or 2500 lbs.). It must be remarked that the connecting tube did not fit satisfactorily, and that at the time (2 o'clock) a small gas jet was burning in the room. At 4.25 the explosion occurred, but as no one had been in the drawing office but Mr. Bewley himself the conditions under which the explosion took place are not precisely known. The evidence, however, is fairly conclusive.

In the first place it must be stated that the metal of the cylinder was perfectly sound, and in the interior there was no appearance either of oil or of rust. While the upper part of the cylinder was blown to pieces, the body of it struck the arch over a window and caused the wall to bulge; it then ricocheted apparently against the wall, and passed through a window opposite to where it had first struck. The upper end of the cylinder was found at a much greater distance from the building.

One witness, who saw a gauge on the bottle marking 800 lbs., believed that the cylinder had been overcharged, and that disruption occurred simply by the elastic force of the gas. Having examined the premises, I was in a position to state at the inquest that the nature of the explosion was most certainly that of a detonation. The table and drawers were splintered into match-wood, and the glass from the window, as it lay on the ground, presented the peculiarities of fracture which are characteristic of such an explosion.

The examination of the top of the cylinder just below the shoulder showed that the fractured metal at this part had a different appearance from the other fractured surfaces. Instead of being bright it was burnt all the way round, that is to say, covered with magnetic oxide. Moreover, the medical evidence showed that death was caused by shock, and the force of the explosion threw the body out of the room. While the left hand was severed from the arm at four inches above the wrist, the right was charred, and singeing was noticed on the right leg, and the air was crisp from the same cause.

Without doubt the explosion occurred from the detonation of mixed gases within the cylinder.

The valves of both cylinders, which had been connected by a tube previously, were found wide open. The ignition of the gases was most probably caused, not by any chemical action spontaneously taking place within the cylinder, but either by a leakage, which was tested by applying a match, or, the leakage being serious, the gases were fired by a lighted gas jet. It must be remembered that what was believed to be the same gas had previously exploded

in the limelight apparatus, merely blowing off the india-rubber tube, but, the valve being but slightly open, the explosion was not communicated to the interior of the cylinder because the pressure was higher and the issuing gas was travelling at too great a speed for the temperature of ignition to be maintained in the stream issuing from the small orifice in so large a mass of metal.

For the better understanding of this explanation I will refer to a very simple experiment. Carbon monoxide stored in a gas-holder under a pressure of six inches of water cannot be burnt from an ordinary gas jet, but if the size of the orifice is enlarged to 1-16th or 1-8th of an inch it can be made to burn when the pressure is somewhat reduced. There is no material alteration in the conditions of the experiment if the gas be mixed with air or oxygen. In fact, the temperature of ignition cannot be maintained in contact with the cooling mass which surrounds a small orifice, or with the gas under a very rapid rate of flow.

We cannot precisely ascertain the temperature of ignition or the rapidity of explosion of the mixture of gases contained in the cylinder, but it certainly contained a large excess of oxygen, and the conditions under which it was first found to be dangerous were different and less favourable to explosion than after the pressure was reduced.

The verdict of accidental death was coupled with a recommendation that the public should be protected from similar accidents by a Government stamp being fixed to all cylinders used for such purposes. But greater safety would be secured by making the fittings for hydrogen and oxygen cylinders so entirely different that it would be practically impossible to charge a cylinder with wrong gas.

USE OF HYDROGEN PEROXIDE IN ANALYSIS.

By F. P. DUNNINGTON.

LEAD peroxide may be most readily dissolved by treatment with dilute nitric acid and a solution of hydrogen peroxide. Half of the oxygen from each of the two peroxides unite to produce an effervescence of oxygen, even when cold, resulting in the formation of a solution of lead nitrate.

A similar action of hydrogen peroxide, I have frequently found of advantage in effecting the solution of a precipitate produced by ammonia and consisting mainly of ferric and alumina hydrates, in which, however, after washing, a little manganese is retained as Mn_2O_3. The latter body will resist solution in dilute acid, and under these circumstances a drop or two of hydrogen peroxide will instantly clear up the solution.

In the same manner, ignited oxide of cerium or oxide of manganese may be readily dissolved by cold dilute acids mixed with hydrogen peroxide.—*Journal of Analytical Chemistry*, Vol. ii., Part 4.

University of Virginia, Sept. 10, 1888.

THE USE OF AMMONIUM DITHIOCARBAMINATE IN ANALYSIS.

By JOSEPH KLEIN.

AMMONIUM dithiocarbaminate is formed if we pass the ammonia evolved from 150 parts ammonium chloride and 300 parts caustic lime into 600 parts alcohol at 95 per cent, and add to the solution 96 parts carbon disulphide. At 30° ammonium dithiocarbaminate crystallises out alone, and may be collected on a filter, washed with a little alcohol, and dried between blotting-paper. The salt is dissolved in water to a 5 per cent solution, which is very permanent, while the crystals readily decompose.

Determination of Copper.

If a solution of copper sulphate is mixed with the reagent there falls a yellow precipitate of copper dithiocarbaminate. If the solution is hot and is boiled for a few seconds, the precipitate deposits very well. It is soluble on prolonged boiling with an excess of hydrochloric acid, and is decomposed if heated with nitric acid. It is not changed on exposure to the air or on washing. If the precipitate is mixed with sulphur and ignited in a current of hydrogen sulphide it is converted into copper sulphide.

For the quantitative determination of copper the slightly hydrochloric solution is precipitated with ammonium dithiocarbaminate, boiled up, filtered, and washed with hot water; the precipitate is then dried and converted into copper sulphide. No other metals of the fifth group and no metals of the sixth group must be present along with the copper.

Determination of Zinc.

If a solution of zinc sulphate is mixed with ammonium dithiocarbaminate there is formed a white precipitate of zinc dithiocarbaminate soluble in an excess of the precipitant. If the clear solution is then boiled there again occurs precipitation. Zinc dithiocarbaminate is soluble in hydrochloric and nitric acids, but not in acetic acid if the solution is sufficiently dilute. Hence ammonium dithiocarbaminate throws down zinc from a weak acetic solution on gentle heating. On exposure to the air and on washing with hot water zinc dithiocarbaminate undergoes no change. On admixture with sulphur and ignition in a current of hydrogen it is converted into zinc sulphide. On prolonged boiling in an acetic liquid it is decomposed with formation of zinc sulphide, which does not run clear through the filter. Thus, the complete precipitation of zinc as dithiocarbaminate depends on conditions which may be gathered from the following case:—

50 c.c. of a solution of zinc sulphate containing 3·5826 grms. zinc oxide per litre were mixed with a quantity of sodium acetate sufficient for the formation of zinc acetate, 100 c.c. distilled water, and 1 to 1·5 c.c. acetic acid of sp. gr. 1·02. The liquid was heated to a boil and 30 c.c. of a 5 per cent solution of ammonium dithiocarbaminate were added and the boiling was continued for a short time. As soon as no further deposition of the zinc salt took place it was allowed to settle, filtered while still hot, and washed with hot water. The dried precipitate was converted into zinc sulphide.

The filtrate generally passes through clear from the beginning, but it afterwards becomes turbid in consequence of the decomposition of residual ammonium dithiocarbaminate or of sulphuretted hydrogen. When all the filtrate is passed through and the precipitate is washed with hot water we obtain a clear filtrate which no longer becomes turbid. If the filtrate passes through turbid from the beginning some zinc sulphide may have been formed. The filtration is then completed without regarding the turbidity, the precipitate is washed with hot water, the filtrate and washings are concentrated with the addition of a few drops of hydrochloric acid, acidulated with acetic acid, and the remnant of zinc is thrown down with ammonium dithiocarbaminate.

Separation of Copper and Zinc.

The precipitability of copper dithiocarbaminate and the solubility of the corresponding zinc salt might point to the possibility of a direct separation of copper and zinc. Experiment showed, however, that a complete separation of the two metals can be effected only by repeated precipitations, so that the use of ammonium dithiocarbaminate presents no advantage over the ordinary methods.

Behaviour of Ammonium Dithiocarbaminate with Some other Saline Solutions.

Iron, nickel, cobalt, and manganese are not thrown down if the precipitant is added to the hot solutions and sufficient hydrochloric acid is present.

The earthy-alkaline and alkaline dithiocarbaminates are soluble in water. Still, in determining copper in presence of considerable quantities of the alkaline earths or the alkalies, a repeated precipitation of the copper is needful.—*Zeitschrift fur Analytische Chemie* (Vol. xxviii., Part 1, p. 90).

RE-CALCULATIONS OF THE ATOMIC WEIGHTS.*

By F. P. VENABLE.

WITHIN the last five years several attempts have been made by chemists of prominence to re-calculate the many atomic weight determinations upon a uniform basis and by uniform methods, and so secure, if possible, a trustworthy table of these most important constants of nature. Our better knowledge of these elements and the increased accuracy of modern methods promised favourably for the success of such an undertaking. That such a revision was called for a glance at the text-books of the time will abundantly show. The greatest variance was shown in the tables of atomic weights given. They seemed to be chosen most arbitrarily. No single authority was recognised, and in many cases it would have been difficult to trace the source of the numbers given. Especially were the differences notable in text-books of different nationalities. Taking two nearly contemporaneous text-books widely used in England, America, and Germany—Watts (1878) and Richter (1881)—I find that out of 64 elements 37 per cent only have the atomic weights the same in both; 22 per cent differ by from 0·10 to 0·25; 20 per cent differ from 0·25 to 0·50; 10 per cent differ from 0·50 to 1·00; and 11 per cent differ by more than 1, the difference in several cases ranging from 25 to 40.

To call such a list a table of constants seems ridiculous, nor does it speak well for chemistry as a science that these, the very foundation stones on which its building is reared, should be so unstable and little trustworthy. Analyses calculated by numbers so different, as in these two tables, must give very different results, one or the other, or perhaps both, of which must be erroneous.

The evil was and is a crying one, and demands the best energies of the wisest chemists to rectify.

The general acceptation of the Law of Periodicity has been another potent factor in drawing attention to the need for careful revision, and in many cases re-determination, of the atomic weights. Those who have undertaken this revision have met with many serious obstacles which are still very far from being overcome. This, I think, will be seen as we proceed in the discussion of the results obtained.

The Unit or Basis.

The first essential is the adoption of a unit of calculation or basis, and this has proved one of the great obstacles in the way of uniformity. Two elements suggest themselves as bases for these calculations—hydrogen and oxygen. For fifty years or more the strife has raged as to which of these should be adopted. Hydrogen has been practically adopted and used, but the opposition to it has only slumbered at times and seems rising again in the past few years. Dalton and Gmelin were the advocates of the hydrogen unit in early days, and Wollaston and Berzelius advocated oxygen. Among the late revisers and recalculators Becker* refers all the atomic weights to oxygen = 16. Clarke† gives tables calculated either for oxygen = 16 or hydrogen = 1. Sebelien‡ uses the units hydrogen = 1 or oxygen = 100, as also do Meyer and Seubert.§ Ostwald‖ uses hydrogen = 1, giving to oxygen the value 16. Van der Plaats¶ has selected oxygen = 16 as the basis for his re-calculation.

There is a decided predominance of authority in favour of oxygen as the standard and of giving it the value 16, though some would make it appear that this is the same thing as adopting hydrogen = 1.

What points should decide the choice of our unit? They have been ably discussed by Meyer and Seubert,** but I must confess they seem to me somewhat blinded themselves by the partisanship of which they accuse their opponents, and I cannot agree with them in all of their conclusions.

I would state as the essentials for the unit element:

1st. That it must be one with which the greatest number of the other elements can be directly compared, thus avoiding the multiplication of error.

2nd. Its own atomic weight must be reasonably small so as not to make too great the higher atomic weights.

3rd. The atomic weights of the other elements got by comparison with it should be, as many of them as possible, integers, or nearly so, rendering calculation easier. In spite of all the tabular and other aids at the command of the chemist of the present day, calculations with an atomic weight having an awkward fraction cause the loss of much time.

Now on examining with a view to these requisites the two elements proposed as units, oxygen alone will be found to answer every requirement.

Nearly all of the present atomic weights have been determined by the aid of oxygen.

Few can be directly compared with hydrogen, and this forms the almost insuperable objection to hydrogen as a standard.

Hydrogen has been used for the past half century for the two last reasons cited among the requisites. As it has the smallest atomic weight, all the others would be above unity if it were taken as the unit. Thus fractional atomic weights were avoided, and again a large number of the other atomic weights compared with it are approximately integers. I am confidant that this is mainly made use of as a matter of convenience and of custom at the present day, and that no special weight is attached to the coincidences with whole numbers. It did give rise to a visionary sort of hypothesis, first enunciated by the Rev. Mr. Prout in 1815, and hence called Prout's hypothesis, that all of the atomic weights were multiples of that of hydrogen, and, as an inference to be drawn, that hydrogen was the primal element of which they were made.

This hypothesis has had many valiant defenders and a large number of most determined opponents, and it has called forth work that has been of immense benefit to the science. It is well that this one good thing can be spoken of so many false suppositions and theories. As an hypothesis it is based on a few coincidences which were to be naturally looked for in the light of mathematics and the law of probabilities. One may say that no absolute proof in its favour has ever been advanced, nor does it seem capable of proof at the present day. A cursory examination would reveal proportionately similar coincidences for some of the other elements. I say proportionately for, of course, the smaller the atomic weight the greater the number of its multiples, and the greater the probability of coincidences within the limits given.

* From the *Journal of the Elisha Mitchell Scientific Society*, Vol. v., Part 2.

* "Constants of Nature," Part IV., Smithsonian Institution, 1880.
† *Ibid.*, Part V., Smithsonian Institution, 1887.
‡ "Beiträge zur Geschichte der Atomgewichte," 1884.
§ "Die Atomgewichte der Elemente," 1883.
‖ "Lehrbuch der Allgemeinen Chemie," 1885.
¶ *Annales de Chimie et de Physique* (6 serie) 7 April, 1886.
** *Berichte der Deutschen Chem. Gesell.*, xviii., 1089.

TABLE No. I.

Factor.	Multiples of 7·98=¼ O.	Elements.	Differences.	Multiples of 3·52=¼ Li.	Elements.	Differences.	Multiples of 6=¼ C.	Elements.	Differences.
2.	15·96	O	0	7·04	Li	0	12·00	C	0
3.	23·94	Mg	0	10·56	Be	+0·44	18·00	—	—
4.	31·92	S	+0·06	14·08	Ni	−0·04	24·00	Mg	+0·38
5.	39·90	Ca	+0·01	17·60	—	—	30·00	—	—
6.	47·88	Ti	+0·13	21·12	—	—	36·00	Cl	−0·55
7.	55·86	Fe	+0·02	24·64	Mg	−0·26	42·00	—	—
8.	63·84	Cu	−0·66	28·16	Si	−0·10	48·00	Ti	+0·12
9.	71·82	Ge	+0·50	31·68	S	+0·38	54·00	—	—
10.	79·80	Br	−0·04	35·20	Cl	+0·25	60·00	Co	−0·90
11.	87·78	Sr	−0·48	38·72	K	+0·41	66·00	Zn	−0·62
12.	95·76	Mo	+0·14	42·24	—	—	72·00	Ger	+0·32
13.	103·74	Ru	−0·24	45·76	—	—	78·00	—	—
14.	111·72	Cd	0	49·28	—	—	84·00	—	—
15.	119·70	Sb	−0·10	52·80	Cr	−0·50	90·00	Zr	+0·70
16.	127·68	—	—	56·32	Fe	−0·32	96·00	Mo	−0·10
17.	135·66	—	—	58·82	Co	+0·28	102·00	—	—
18.	143·64	—	—	63·36	Cu	−0·03	108·00	Ag	+0·06
19.	151·62	—	—	66·88	—	—	114·00	Ir	−0·30
20.	159·60	—	—	70·40	Ga	−0·50	120·00	Sb	+0·29
21.	167·58	—	—	73·92	—	—	126·00	Te	−0·80
22.	175·56	—	—	77·44	—	—	132·00	Cs	+0·88
23.	183·54	W	+0·06	80·96	—	—	138·00	La	+0·50
24.	191·52	—	—	84·48	—	—	144·00	—	—
25.	199·50	Hg	+0·30	88·00	Sr	−0·48	150·00	Sm	+0·20
26.	207·48	Bi	−0·18	91·52	Zr	−0·92	156·00	—	—
27.	215·46	—	—	95·04	Mo	+0·86	162·00	—	—
28.	223·44	—	—	98·56	—	—	168·00	—	—
29.	231·42	Th	+0·54	102·08	—	—	174·00	Yb	−0·80
30.	239·40	U	+0·40	105·60	Pb	−0·60	180·00	—	—
31.	—	—	—	109·12	—	—	186·00	—	—
32.	—	—	—	112·64	Cd	−0·56	192·00	—	—
33.	—	—	—	116·16	—	—	198·00	—	—
34.	—	—	—	119·68	Sb	+0·61	204·00	Tl	+0·15
35.	—	—	—	123·20	—	—	210·00	—	—
36.	—	—	—	126·72	I	+0·14	216·00	—	—
37.	—	—	—	129·24	—	—	222·00	—	—
38.	—	—	—	132·76	Cs	+0·12	228·00	—	—
39.	—	—	—	136·28	Ba	+0·76	234·00	Th	−1·00
40.	—	—	—	140·80	Ce	+0·70	240·00	U	−1·00
41.	—	—	—	144·32	Di	+0·68	—	—	—
49.	—	—	—	172·48	Yb	+0·72	—	—	—
52.	—	—	—	183·14	Ta	−0·34	—	—	—
55.	—	—	—	193·70	Ir	−0·59	—	—	—
56.	—	—	—	197·22	Au	−0·48	—	—	—
57.	—	—	—	200·74	Hg	−0·30	—	—	—
58.	—	—	—	204·26	Tl	−0·11	—	—	—
59.	—	—	—	207·78	Bi	+0·23	—	—	—
62.	—	—	—	218·34	Ng	+0·66	—	—	—
68.	—	—	—	239·46	U	+0·54	—	—	—

I cannot believe that Meyer and Seubert* are serious when they state it as a "striking fact that the atomic weights of more than one-fourth of all the elements are very nearly multiples of the half atomic or equivalent weight of oxygen," giving a table to show this, and adding that "such regularities are worthy of note." They can scarcely be worthy of much note, for such regularities or coincidences would be exceedingly probable where we have sixty or seventy elements with atomic weights under 240, and take a small number with thirty or more multiples in the same range. The smaller the number the more numerous will be the multiples, and consequently the coincidences. To show this I have added to the table of Meyer and Seubert two other lists of multiples and "regularities."

I cannot think that these authors really mean this as in any way a plea for oxygen=15·96. It must be intended to show the ridiculous nature of the grounds upon which Prout's hypothesis has been based. Certainly they are correct in their deduction that "to attempt to correct the atomic weights by them (*i.e.*, these regularities) would be just as incorrect as to round them off into whole numbers." With such glaring and persistent exceptions as chlorine, chromium, copper, strontium, gold, and others, the hypothesis of Prout must fail to take its place as a law, since no law could be accepted with so large a percentage of exceptions.

It is not necessary to discuss the modifications of Prout's hypothesis which have been proposed—the half-atom or fourth-atom of hydrogen as unit, &c. Such changes really do away with all meaning to the hypothesis, and the valuable idea which Meyer and Seubert acknowledge may lie concealed in it, is lost.

That the hypothesis is still doing yeoman's service to science is shown by the number of new determinations, within the past two years, of the ratio between hydrogen and oxygen. It is evidence of the struggle to retain the old unit hydrogen, and at the same time secure accuracy for it by fixing definitely its relation to oxygen, by means of which nearly all comparisons with the other elements must be made. I fear that much of this work would not have been done if it had been made to appear that the

* *Loc. cit.*

atomic weight of hydrogen, and not of oxygen, was aimed at. The atomic weight of hydrogen has only the ordinary interest of that of any of the elements. With the atomic weight of oxygen they all stand or fall, no matter which we choose as our theoretical unit. The new determinations referred to are—

Rayleigh (Chemical News, vol. lvii., p. 73), O = 15·912.

Cooke and Richards (*Am. Chem. Journal*, vol. x., p. 81), O = 15·953.

Cooke and Richards (*Am. Chem. Journal*, vol. x., p. 91), O = 15·869.

Keiser (*Am. Chem. Journal*, vol. x., p. 250), O = 15·949.

None of them come up, indeed, to the present assumption of O = 15·96, so if these investigators are correct, or more nearly correct than those who have preceded them, the whole table of atomic weights must be again shifted.

It is time then that hydrogen were finally discarded as the unit. Oxygen is in every way preferable, and nothing like uniformity will be attained until it is adopted.

With oxygen as the standard, what value shall be assigned to it? Four values have been suggested: 1st, O = 1; 2nd, O = 10; 3rd, O = 16; 4th, O = 100.

If O = 1 we should have nearly 10 per cent of the elements represented by decimal fractions, and the following partial table would show other inconveniences:—

Al	.. ..	1·694	Cr	.. ..	3·284
F	.. ..	1·194	Fe	.. ..	3·501
Mg	.. ..	1·500	Co	.. ..	3·67
Na	.. ..	1·4408	Cu	.. ..	3·95
P	.. ..	1·940	Mn	.. ..	3·43
S	.. ..	2·0037	Ni	.. ..	3·67
			Ti	.. ..	3·15
Si	.. ..	1·754	V	.. ..	3·20

The differences between the elements are too small for speedy recognition or for easy memorising. O = 1 is manifestly too small.

Considering next the fourth suggestion, O = 100, we see that just the opposite objection holds good. Over one-fifth of the elements would be represented by numbers exceeding 1000. Few of these could be accurately given as far as the fourth place. For instance, shall gold be represented by the number 1229·4, or 1225·1, or 1234·0, or 1249·0, all of which are actual determinations? From long custom we have come to regard a whole number as being correct and the decimals as indicating approximations. It would seem to be best still to hide our imperfections under the decimals.

The only claim that can be adduced in favour of O = 10 is that we will then have the atomic weights on the decimal system. This is not true, however, unless the other atomic weights are multiples of ten. A glance at a few of the elements will show that the numbers would be complicated, rather than simplified, by such an unit.

H	= 6·265	F	= 11·94
Li	= 4·39	Na	= 14·408
Be	= 5·89	Fe	= 35·01
B	= 6·83	Co	= 36·70
C	= 7·502	Mn	= 34·30
N	= 8·779	Cu	= 39·50

That is, the eight first elements, which in our present tables are approximately whole numbers, and in ordinary calculations commonly taken as such (especially in technical analyses, and we must not let theoretical considerations take us out of sight of the practical side of chemistry), are, when compared with O = 10, burdened with cumbrous fractions and brought inconveniently near to one another. This last consideration is of especial weight when the clearness of the Periodic Law is considered.

There remains then only O = 16 to be considered. The advantage of this unit may be summed up as follows:—

1st. Every atomic weight is above unity and yet not inconveniently large.

2nd. The distance between the atomic weights renders them easy to memorise, and is more convenient for the illustration of the "Periodic Law."

3rd. About two-thirds of the atomic weights are either whole numbers or vary from whole numbers by fractions of $\frac{1}{10}$ or less.

4th. The adoption of this as a unit practically means the retention of most of the numbers so long in use. The valuable literature of the past three or four decades need not be rendered less useful and intelligible to the chemists of the present and the future, as it would be by radical changes in these combining numbers.

Some chemists seem to feel an especial repugnance to this unit because it is too arbitrary and unusual, not bearing upon its face the fact that it is the unit, and again because hydrogen is then represented by the number 1·0025. The arbitrariness of it seems unavoidable: as to why they should be troubled by the number given hydrogen is not very apparent. The fraction is an easy one to handle and may often be neglected. It can make no possible difference in the close calculations of organic chemistry cited by Meyer and Seubert, whether H = 1 and O = 15·96 or H = 1·0025 and O = 16. The only thing is to keep the ratio which most exact research reveals as existing between the two. The tendency of the day is toward O = 16, and it should be universally adopted. To avoid dangerous assumptions the other atomic weights should be rigidly put down in accord with the most accurate determinations available. This brings us to consider another difficulty and cause of variation.

(To be continued).

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 70).

Methods for the Determination of Nitrogen.

The Absolute or Cupric Oxide Method.

(Applicable to all nitrogen determinations).

The apparatus and reagents needed are as follows:—

Apparatus.

Combustion tube of best hard Bohemian glass, about 26 inches long and one-half inch internal diameter.

Azotometer of at least 100 c.c. capacity, accurately calibrated.

Sprengel mercury air-pump.

Small paper scoop, easily made from stiff writing-paper.

Reagents.

Cupric Oxide (coarse).—Wire form; to be ignited and cooled before using.

Fine Cupric Oxide.—Prepared by pounding ordinary cupric oxide in mortar.

Metallic Copper.—Granulated copper or fine copper gauze reduced and cooled in stream of hydrogen.

Sodium Bicarbonate.—Free from organic matter.

Caustic Potash Solution.—Dissolve commercial stick potash in less than its weight of water so that crystals are deposited on cooling. When absorption of carbonic acid ceases to be prompt solution must be discarded.

Loading Tube.

Of ordinary commercial fertilisers take 1 to 2 grms. for analysis. In the case of highly nitrogeneous substances the amount to be taken must be regulated by the amount

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

of nitrogen estimated to be present. Fill tube as follows :—(1). About 2 inches of coarse cupric oxide. (2). Place on the small paper scoop enough of the fine cupric oxide to fill, after having been mixed with the substance to be analysed, about 4 inches of the tube; pour on this the substance, rinsing watch-glass with a little of the fine oxide, and mix thoroughly with spatula; pour into tube, rinsing the scoop with a little fine oxide. (3). About 12 inches of coarse cupric oxide. (4). About 3 inches of metallic copper. (5). About 2½ inches of coarse cupric oxide (anterior layer). (6). Small plug of asbestos. (7). Eight-tenths to 1 grm. of sodium bicarbonate. (8). Large, loose plug of asbestos; place tube in furnace, leaving about 1 inch of it projecting; connect with pump by rubber stopper smeared with glycerin, taking care to make connection perfectly tight.

Operation.

Exhaust air from tube by means of pump. When a vacuum has been obtained allow flow of mercury to continue, light gas under that part of tube containing metallic copper, anterior layer of cupric oxide (see 5th above), and bicarbonate of soda. As soon as vacuum is destroyed and apparatus filled with carbonic acid gas, shut off the flow of mercury and at once introduce the delivery tube of the pump into the receiving arm of the azotometer, and just below the surface of the mercury seal off the azotometer, so that the escaping bubbles will pass into the air and not into the azotometer, thus avoiding the useless saturation of the caustic potash solution.

When the flow of carbonic acid has very nearly or completely ceased, pass the delivery tube down into the receiving arm, so that the bubbles will escape into the azotometer. Light the jets under the 12-inch layer of oxide, heat gently for a few moments to drive out any moisture which may be present, and bring to red heat. Heat gradually mixture of substance and oxide, lighting one jet at a time. Avoid too rapid evolution of bubbles, which should be allowed to escape at rate of about one per second or a little faster.

When the jets under mixture have all been turned on, light jets under layer of oxide at end of tube. When evolution of gas has ceased turn out all the lights except those under the metallic copper and anterior layer of oxide, and allow to cool for a few moments. Exhaust with pump, and remove azotometer before flow of mercury is stopped. Break connection of tube with pump, stop flow of mercury, and extinguish lights. Allow azotometer to stand for at least an hour or cool with stream of water until permanent volume and temperature are reached.

Adjust accurately the level of the KOH solution in bulb to that in azotometer, note volume of gas, temperature, and height of barometer; make calculations as usual. The labour of calculation may be much diminished by the use of the tables prepared by Messrs. Battle and Dancy, of the North Carolina Experiment Station (Rayleigh, N.C).

The above details are, with some modifications, those given in the *Report of the Connecticut Station* for 1879, (p. 124), which may be consulted for details of apparatus, should such details be desired.

The Kjeldahl Method.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

(1). Hydrochloric acid, whose absolute strength has been determined (*a*) by precipitating with silver nitrate and weighing the silver chloride, (*b*) by sodium carbonate, as described in Fresenius's "Quantitative Analysis," second American edition, page 680, and (*c*) by determining the amount neutralised by the distillate from a weighed quantity of pure ammonium chloride boiled with an excess of sodium hydrate. Half normal acid, *i.e.*, containing 18·25 grms. hydrochloric acid to the litre, is recommended.

(2). Standard ammonia whose strength, relative to the acid, has been accurately determined. One-tenth normal ammonia, *i.e.*, containing 1·7 grms. ammonia, to the litre, is recommended for accurate work.

(3). "C. P." sulphuric acid, specific gravity 1·83, free from nitrates and also from ammonium sulphate, which is sometimes added in the process of manufacture to destroy oxides of nitrogen. Eimer and Amend's "Strictly C. P." is good.

(4). Mercuric oxide, HgO, prepared in the wet way. That prepared from mercury nitrate cannot safely be used.

(5). Potassium permanganate tolerably finely pulverised.

(6). Granulated zinc.

(7). A solution of 40 grms. of commercial potassium sulphide in one litre of water.

(8). A saturated solution of sodium hydrate free from nitrates, which are sometimes added in the process of manufacture to destroy organic matter and improve the colour of the product. That of the Greenbank Alkali Company is of good quality.

(9). Solution of cochineal prepared according to Fresenius's "Quantitative Analysis," second American edition, page 679.

(10). Kjeldahl digestion flasks of hard, moderately thick, well annealed glass. These flasks are about 9 inches long, with a round, pear-shaped bottom, having a maximum diameter of 2½ inches, and tapering out gradually in a long neck, which is three-fourths of an inch in diameter at the narrowest part, and flared a little at the edge. The total capacity is 225 to 250 c.c.

(11). Distillation flasks of ordinary shape, 550 c.c. capacity, and fitted with a rubber stopper and a bulb tube above to prevent the possibility of sodium hydrate being carried over mechanically during distillation. The bulbs are about 1¼ inches in diameter, the tubes being the same diameter as the condenser and cut off obliquely at the lower end. This is adjusted to the tube of the condenser by a rubber tube.

(12). *A Condenser.*—Several forms have been described, no one of which is equally convenient for all laboratories. The essential thing is that the tube which carries the steam to be condensed shall be of block-tin. The upper ends of the tin tubes should be bent so that the glass connections may have a slope towards the distilling flasks. All kinds of glass are decomposed by steam and ammonia vapour, and will give up alkali enough to impair accuracy. (See Kreussler and Henzold, *Berichte*, xvii., 34). The condenser in use in the laboratory of the Connecticut Experiment Station, devised by Professor Johnson, consists of a copper tank, supported by a wooden frame, so that its bottom is 11 inches above the work-bench on which it stands. This tank is 16 inches high, 32 inches long, and 3 inches wide from front to back, widening above to six inches. It is provided with a water supply tube, which goes to the bottom, and a larger overflow pipe above. The block-tin condensing tubes, whose external diameter is three-eighths of an inch, seven in number, enter the tank through holes in the front side of it near the top, above the level of the overflow, and pass down perpendicularly through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 1¼ inches below the bottom of the tank, and are connected by short rubber tubes with glass bulb tubes of the usual shape, which dip into precipitating beakers or Erlenmeyer flasks of about 300 c.c. capacity. The titration can be made directly in them. The distillation flasks are supported on a sheet-iron shelf, attached to the wooden frame that supports the tanks in front of the latter. Where each flask is to stand a circular hole is cut, with three projecting lips, which support the wire gauze or asbestos under the flask, and three other lips, which hold the flask in place and prevent its moving laterally out of place while distillation is going on. Below this sheet-iron shelf is a metal tube carrying seven Bunsen burners, each with a stop-cock like those

of a gas-combustion furnace. These burners are of a larger diameter at the top, which prevents smoking when covered with a fine gauze to prevent the flame from striking back.

(13). The stand for holding the digestion flasks consists of a pan of sheet-iron 29 inches long by 8 inches wide, on the front of which is fastened a shelf of sheet-iron as long as the pan, 5 inches wide and 4 high. In this are cut six holes 1½ inches in diameter. At the back of the pan is a stout wire running lengthwise of the stand, 8 inches high, with a bend or depression opposite each hole in the shelf. The digestion flask rests with its lower part over a hole in the shelf and its neck in one of the depressions in the wire frame, which holds it securely in position. Heat is supplied by low Bunsen burners below the shelf. With a little care the naked flame can be applied directly to the flask without danger.

The Determination.

(1). *The Digestion.*—Seven-tenths to 2·8 grms. of the substance to be analysed, according to its proportion of nitrogen, is brought into a digestion flask with approximately 0·7 grm. of mercuric oxide and 20 c.c. of sulphuric acid. The flask is placed on the frame above described in an inclined position, and heated below the boiling-point of the acid for from five to fifteen minutes, or until frothing has ceased. If the mixture froths badly, a small piece of paraffin may be added to prevent it. The heat is then raised until the acid boils briskly. No further attention is required until the contents of the flask have become a clear liquid, which is colourless, or at least has only a very pale straw colour. The flask is then removed from the frame, held upright, and, while still hot, potassium permanganate is dropped in carefully and in small quantity at a time till, after shaking, the liquid remains of a green or purple colour.

(2). *The Distillation.*—After cooling, the contents of the flask are transferred to the distilling flask with about 200 c.c. of water, and to this a few pieces of granulated zinc and 25 c.c. of potassium sulphide solution are added, shaking the flask to mix its contents. Next add 50 c.c. of the soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all of the ammonia. This operation usually requires from forty minutes to one hour and a half. The distillate is then titrated with standard ammonia.

The use of mercuric oxide in this operation greatly shortens the time necessary for digestion, which is rarely over an hour and a half in cases of substances most difficult to oxidise, and is more commonly less than an hour. In most cases the use of potassium permanganate is quite unnecessary, but it is believed that in exceptional cases it is required for complete oxidation, and in view of the uncertainty it is always used. Potassium sulphide removes all mercury from solution, and so prevents the formation of mercuro-compounds which are not completely decomposed by soda solution. The addition of zinc gives rise to an evolution of hydrogen and prevents violent bumping. Previous to use the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates that are present which might otherwise escape notice.

Kjeldahl Method Modified to Include the Nitrogen of Nitrates.*

(Applicable to all fertilisers containing nitrates).

Besides the reagents and apparatus given under the Kjeldahl method there will be needed—

(1). Zinc dust. This should be an impalpable powder; granulated zinc or zinc filings will not answer.

(2). Commercial salicylic acid.

The Determination.

Bring from 0·7 to 1·4 grms. of the substance to be analysed into a Kjeldahl digesting flask, add to this 30 c.c. of sulphuric acid containing 2 grms. of salicylic acid, and shake thoroughly; then add *gradually* 3 grms. of zinc dust, shaking the contents of the flask at the same time. Finally place the flask on the stand for holding the digestion flasks, where it is heated over a low flame until all danger from frothing has passed. The heat is then raised until the acid boils briskly, and the boiling continued until white fumes no longer pour out of the flask. This requires about five or ten minutes. Add now approximately 0·7 grm. mercuric oxide, and continue the boiling until the liquid in the flask is colourless, or nearly so. (In case the contents of the flask are likely to become solid before this point is reached, add 10 c.c. more sulphuric acid). Complete the oxidation with a little permanganate of potash in the usual way, and proceed with the distillation as described in the Kjeldahl method. The reagents should be tested by blank experiments.

The Ruffle Method.

Apparatus and Reagents.

(1). Standard solutions and indicator the same as for the Kjeldahl method.

(2). A mixture of equal parts by weight of fine soda-lime and finely powdered, crystallised sodium hyposulphite.

(3). A mixture of equal parts by weight of finely powdered granulated sugar and flowers of sulphur.

(4). Granulated soda-lime, as described under the soda-lime method.

(5). Combustion-tubes of hard Bohemian glass, 20 inches long and ½ inch in diameter.

(6). Bulbed "U" tubes or Wills's bulbs, as described under the soda-lime method.

Preparation.

(1). Clean and fill the U-tube with 10 c.c. of standard acid.

(2). Fit cork and glass connecting tube. Fill the tube as follows:—(1). A loosely fitting plug of asbestos, previously ignited, and then 1 to 1½ inches of the hyposulphite mixture. (2). The weighed portion of the substance to be analysed is intimately mixed with from 5 to 10 grms. of the sugar and sulphur mixture. (3). Pour on a piece of glazed paper, or porcelain mortar, a sufficient quantity of the hyposulphite mixture to fill about 10 inches of the tube; then add the substance to be analysed, as previously prepared; mix carefully and pour into the tube; shake down the contents of the tube; rinse off the paper or mortar with a small quantity of the hyposulphite mixture and pour into the tube; then fill up with soda-lime to within 2 inches of the end of the tube. (4) Place another plug of ignited asbestos at the end of the tube, and close with a cork. (5). Hold the tube in a horizontal position, and tap on the table until there is a gas channel all along the top of the tube. Make connection with the U-tube containing the acid, aspirate, and see that the apparatus is tight.

The Combustion.—Place the prepared combustion-tube in the furnace, letting the open end project a little so as not to burn the cork. Commence by heating the soda-lime portion until it is brought to a full red heat. Then turn on slowly jet after jet toward the outer end of the tube, so that the bubbles come off two or three a second. When the whole tube is red hot and the evolution of the gas has ceased and the liquid in the U-tube begins to recede towards the furnace, attach the aspirator to the other limb of the U-tube, break off the end of the tube, and draw a current of air through for a few minutes. Detach the U-tube and wash the contents into a beaker

* Described by Prof. M. A. Scovell.

or porcelain basin, add a few drops of the cochineal solution, and titrate.

The Soda-Lime Method.

(Not applicable in presence of nitrates).

Apparatus and Reagents.

(1). Standard solutions and indicator the same as for the Kjeldahl method.

(2). Granulated soda-lime, fine enough to pass a 10-mesh sieve, and thoroughly dry.

(3). Fine soda-lime, fine enough to pass a 20-mesh sieve, also thoroughly dry.

To prepare soda-lime of the required fineness, the coarse granulated article of the trade may be ground until it will pass through a sieve of about 0·10-inch mesh. It is then sifted on a sieve of about 0·20-inch mesh to separate the fine from the coarse. The two portions are then thoroughly dried in the air-bath or by heating in a porcelain dish or iron pan over a lamp, stirring constantly.

Excellent soda-lime may be easily and cheaply prepared according to the directions of Professor Atwater (*Am. Chem. Journal*, vol. ix., p. 312) by slaking 2½ parts of quick-lime with a strong solution of 1 part commercial caustic soda (such soda as is used in the Kjeldahl process), care being taken that there is enough water in the solution to slake the lime. The mixture is then dried and heated in an iron pot to incipient fusion, and, when cold, ground and sifted as above.

Instead of soda-lime, Johnson's mixture of carbonate of soda and lime or slaked lime may be used.

Slaked lime may be granulated by mixing it with a little water to form a thick mass, which is dried in the water-oven until hard and brittle. It is then ground and sifted as above. Slaked lime is much easier to work with than soda-lime, and gives excellent results, though it is probable that more of it should be used in proportion to the substance to be analysed than is the case with soda-lime.

(4). Asbestos which has been ignited and kept in a glass-stoppered bottle.

(5). Combustion tubes about 40 c.m. long and about 12 m.m. internal diameter, drawn out to a point and closed at one end.

(6). Large bulbed "U" tubes with glass stop-cock, or Wills tubes with four bulbs.

The Determination.

The substance to be analysed should be powdered fine enough to pass through a sieve of 1 m.m. mesh; 0·7 to 1·4 grms., according to the amount of nitrogen present, is taken for the determination. Into the closed end of the combustion-tube put a small loose plug of asbestos, and upon it about 4 c.m. of fine soda-lime. In a porcelain dish or mortar mix the substance to be analysed, thoroughly but quickly, with enough fine soda-lime to fill about 16 c.m. of the tube, or about 40 times as much soda-lime as substance, and put the mixture into the combustion-tube as quickly as possible by means of a wide-necked funnel, rinsing out the dish and funnel with a little more fine soda-lime, which is to be put in on top of the mixture. Fill the rest of the tube to about 5 c.m. of the end with a granulated lime, making it as compact as possible by tapping the tube gently while held in a nearly upright position during the filling. The layer of granulated soda-lime should not be less than 12 c.m. long. Lastly, put in a plug of asbestos about 2 c.m. long, pressed rather tightly, and wipe out the end of the tube to free it from adhering soda-lime.

Connect the tube by means of a well-fitting rubber stopper or cork with the "U" tube or Wills bulbs, containing 10 c.c. standard acid, and adjust it in the combustion furnace so that the end projects about 4 c.m. from the furnace, supporting the "U" tube or Wills tube suitably. Heat the portion of the tube containing the granulated soda-lime to moderate redness, and when this is attained, extend the heat gradually through the portion containing the substance, so as to keep up a moderate and regular flow of gases through the bulbs, maintaining the heat of the first part until the whole tube is heated uniformly to the same degree. Keep up the heat until gases have ceased bubbling through the acid in the bulbs and the mixture of substance and soda-lime has become white or nearly so, which shows that the combustion is finished. The combustion should occupy about three-quarters of an hour, or not more than one hour. Remove the heat, and when the tube has cooled below redness, break off the closed tip and aspirate air slowly through the apparatus for two or three minutes to bring all the ammonia into the acid. Disconnect, wash the acid into a beaker or flask, and titrate with the standard alkali.

During the combustion, the end of the tube projecting from the furnace must be kept heated sufficiently to prevent the condensation of moisture, yet not enough to char the stopper. The heat may be regulated by a shield of tin slipped over the projecting end of the combustion-tube.

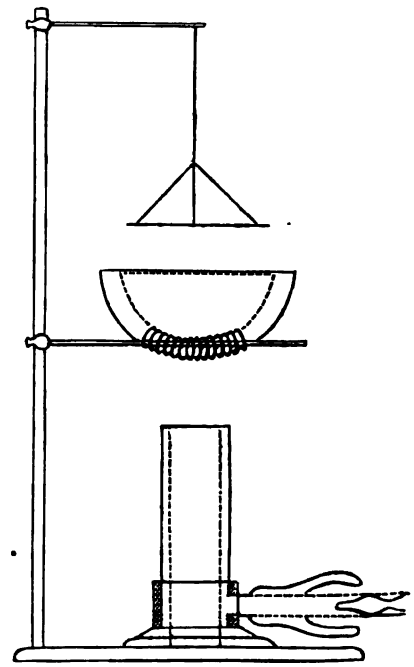
It is found very advantageous to attach a Bunsen valve to the exit tube, allowing the evolved gases to pass out freely, but preventing a violent "sucking back" in case of a sudden condensation of steam in the bulbs.

(To be continued).

ON THE "LOSS ON IGNITION" IN WATER ANALYSIS.

By THOMAS M. DROWN, M.D.

The loss of weight resulting from the ignition of the total solid residue of evaporation of a water was, before the introduction of modern methods of water analysis, supposed to represent the amount of organic matter present



in the water. It is now known that this loss, as ordinarily obtained, by heating the platinum dish containing the residue with the free flame of a Bunsen burner, is a very uncertain quantity. Two chemists will often get widely

different results, in consequence of varying practice in the temperature employed and the time of heating.

In order to eliminate this personal equation, as well as to control the temperature of the ignition, I make use of a large platinum dish as a radiator, inside of which the dish containing the residue is heated.

The accompanying sketch shows the arrangement. The radiator is 4½ inches in diameter and 2 inches deep. The dish in which the water residue is heated is one inch less in diameter, and rests on a coil of platinum wire, half an inch high. A triangle of platinum wire may be used instead of the coil. A flat disk of platinum foil is suspended one inch over the inner dish, in order to radiate back the heat and hasten the combustion of the organic matter. The radiator is maintained at a moderate red heat by means of an argand gas-burner.

Careful experiments have proved that when solutions of sodium chloride, potassium nitrate, and calcium carbonate, either alone, or in solution together, are evaporated to dryness and heated in this way for half an hour or more, there is no loss in weight. When carbonaceous matter, like sugar, is burned off in the presence of calcium carbonate, the latter loses no carbon dioxide. Organic matter would doubtless decompose nitrates, but the quantity of nitrates present in surface waters is so small that the weight of the fixed solid residue would seldom be affected by their partial or entire decomposition. In fact, nitrates are to some extent reduced to nitrites by the heat of the radiator alone, when no organic matter is present; but the amount of this reduction is generally too slight to be appreciated by the balance.

The following determinations were made on the same sample of filtered Cochituate water, in order to compare the loss on ignition in the radiator with that obtained by cautiously heating the dish to dull redness with the Bunsen burner held in the hand. In both cases the brown residue of evaporation was heated until the carbonaceous matter was completely burned off, leaving a white residue; and after this ignition, the residue was moistened with a dilute solution of ammonium carbonate, dried, and the residue again very gently heated to drive off the excess of ammonium salt.

Amount taken.	Loss in radiator.	Loss over free flame.
	Parts per 100,000.	
100 c.c.	1·20	2·00
200 ,,	1·10	1·95
200 ,,	1·10	1·75
200 ,,	1·15	1·65
500 ,,	1·10	1·70
1000 ,,	1·17	1·77
1100 ,,	1·18	1·68

These results show that not only is the loss much lower in the radiator, but that it is much more uniform.

It has been found that moistening the ignited residue with ammonium carbonate solution is unnecessary when the ignition is carried out in the radiator, since no carbon dioxide is driven off; moistening with water and drying at 100° C. answers the purpose—restoring any water of combination which may have existed in the total residue—quite as well.

The determination of the total solid residue and loss on ignition in ground waters is an entirely different problem from that presented in surface waters. In uncontaminated ground waters there is little or no organic matter, and the mineral matters, consisting in part, it may be, of lime, magnesia, chlorine, and nitric acid, are generally present in large amount. On the evaporation of a solution of this character to dryness there is loss of chlorine due to the decomposition of the magnesium chloride, and the solid residue is difficult to weigh owing to its deliquescence. On ignition there is loss of water of crystallisation and of chlorine and nitric acid: indeed, the "loss on ignition" under these circumstances bears no relation whatever to organic matter.

This difficulty can be remedied by adding an amount of sodium carbonate solution, of known strength, to the water in the platinum dish before evaporation, sufficient to make it slightly alkaline. The lime and magnesia are then precipitated as carbonates—compounds which are not deliquescent, do not contain any water of crystallisation, and are permanent at the temperature to which they are exposed in the radiator. The chlorine and nitric acid combine with the alkali and give compounds which are likewise permanent. When the "loss on ignition" is obtained under these conditions in ground waters or in the effluents from the purification of sewage by filtration, it will represent approximately the organic matter. In good ground waters the loss is nothing. The amount of sodium carbonate added is, of course, to be deducted from the weight of the total and fixed residue.

One cannot expect the same sharpness of results in determining the solid matters and loss on ignition in water analysis as is obtained in the determination of the nitrogen compounds. If 200 c.c. of water are taken for evaporation, an error of weight of one milligrm. is equivalent to 0·5 part in 100,000. When we consider the number of conditions which may affect the weight of the residue of evaporation, both before and after ignition,—such as the temperature of the air-bath, the time of heating, the character of the residue, the hygroscopic condition of the atmosphere, the condition of the air of the laboratory, whether containing much dust, or acid or ammoniacal fumes,—the lack of agreement among chemists in this simple determination is not surprising.

The practice in the chemical department of the Massachusetts Institute of Technology is as follows:—200 c.c. of a surface water, or 100 of a ground water which contains considerable mineral contents in solution, are evaporated to dryness on a water-bath in a hood which is used for no other purpose. To the ground water is added, if necessary, sodium carbonate, as above described. When the water is all evaporated the platinum dish is placed in the air-bath, connected with the water-bath, for about one hour. The temperature of this air-bath is 95° to 98° C. The dish is then transferred to a desiccator and cooled over sulphuric acid for half an hour: it matters not how long it stays in the desiccator after it is cool. It is then weighed, and in order that the residue may not absorb moisture during weighing, there are placed in the balance case four beakers of sulphuric acid, which is frequently renewed. This is essential in those cases in which the residue has a tendency to absorb moisture. The dish is next heated in the radiator until all the organic matter is burned off, moistened with water, and put again into the air-bath, that it may be at the second weighing precisely under the conditions as at the first weighing.

The loss of weight in surface waters, which blacken on ignition, may, under these conditions, be regarded as a close approximation to the organic matter present, both vegetable and animal; and the residue or "fixed solids" represents fairly well the mineral matters of the water.—*Technology Quarterly*, Dec., 1888.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Moniteur Scientifique, Quesneville.
December, 1888.

Improvements Effected in the First Half of 1888 in Dyeing and Printing.—Dr. P. Julius.—This valuable paper is too extensive for useful abridgment.

The Chemical Reactions in the Ammonia-Soda Process.—H. Schreib.—This paper will be inserted in full as soon as practicable.

Process of Purification for Alcoholic Liquids and Especially for Spirituous Liquous.—Dr. J. Traube.—A detailed specification of a German patent.

Session of the Academy of Medicine, October 16, 1888.—The conclusion of a medical discussion on the poisonous character of alcohol, on the higher alcohols, and on the artificial bouquets.

The Non-Explosive Character of Commercial Kerosene Oils.—Spencer B. Newbury and W. P. Cutter.—From the *American Chemical Journal.*

Use of Oxygenated Water for Bleaching Wool, Wood, &c.—Alf. Delmart and P. Ebell.—The oxygenated water of the firm of Haen contains very small quantities of foreign bodies, *e.g.*, barium phosphate, but these impurities have a favourable action, as absolutely pure hydrogen peroxide has less bleaching power. The wool is treated in a cold bath, working in a wooden tub. The room should be cool but not exposed to frost during the winter. The wools must be perfectly scoured. The oxygenated water may either be used pure or may be diluted with five to six volumes of rain-water. A little ammonia is added, about 20 grms. of sp. gr. 0·910 to 100 litres. A slip of red litmus-paper should be turned very slightly blue in a few seconds. The wool should not be left heaped up in the bath, but should be turned continually. The process may last from five to six hours. The colouring-matter is totally destroyed, so that the wool does not become yellow in course of time like that which has been bleached with sulphurous acid. P. Ebell contradicts the assertion of Delmart that a pure oxygenated water is less effective than such as contains barium phosphate, which, if present, must be precipitated on the addition of ammonia. He denies also that a cold bath is always necessary, and he maintains that dilution is not advantageous, the liquid, as supplied, containing 3 per cent of actual hydrogen peroxide, giving the best results. —(*Chemiker Zeitung*).

Recent Researches on the Fulminates.—H. N. Warren.—From the Chemical News.

On Griqualandite.—B. H. Brough.—From the Chemical News.

Determination of Microbia in Air.—Prof. Carnelley and Ch. Wilson.—From the Chemical News.

Detection of Iron in Turkey-red Oils.—Dr. B. Ernde.—The author agitates in a graduated cylinder 100 c.c. of the oil along with water acidified with sulphuric acid (100 c.c. of water and 100 c.c. of sulphuric acid), adding a few drops of solution of ferrocyanide. He then adds 25 to 50 c.c. of ether and agitates again. The solution of oil in ether separates readily from the aqueous liquid, and at the line of contact there appears a stratum of Prussian blue.—(*Zeitschrift angew. Chimie*).

Accidental Presence of Mercury in Commercial Tin.—E. Kayser.—The tin used in a manufactory at Nürnberg was found to contain 1·3 per cent of mercury. All the ingots bore the well-known "lamb" brand of S. A. Stone and Sons. This dangerous fraud had been committed in Germany, where a dealer had bought up the waste from a looking-glass works and had melted it down, and apparently had marked it with Messrs. Stone's brand.—(*Chemiker Zeitung*).

Volumetric Determination of Stannous Salts.—Dr. A. Jones.—The author titrates with a solution of permanganate made by dissolving 4 to 5 grms. permanganate and 8 to 10 grms. caustic potassa in 1 litre of water. To standardise this test-liquor he measures exactly 5 to 10 c.c. and adds a solution containing exactly 10 grms. of tartar emetic per litre until the green colour turns to a light brownish yellow. For the determination 0·2 to 0·4 grm. of tin crystals or half the quantity of metallic tin is dissolved in hydrochloric acid in a current of carbonic acid gas. The solution is made up exactly to 250 c.c. 5 or 10 c.c. of the permanganate liquid are put in a test-glass, and the solution of tin is let flow in gently until the change of colour is observed. The liquid must be kept alkaline and in case of need a few c.c. of caustic potassa must be added. For the calculation we have 1 mol. tin salt = 1 mol. permanganate = 1 mol. tartar emetic.—(*Chemiker Zeitung*).

Antimony Mordant with Whey.—M. Kretzschmar.—The author dissolves the antimony mordant in the whey from cheese works, removing the albuminous matters in the usual manner. The liquid is then filtered whilst still hot and abandoned to the lactic fermentation. For use it is diluted with 13 vols. of water and furnishes a mordant equivalent to that given by dissolving 5 grms. of tartar emetic per litre.—(*Chemiker Zeitung*).

The Alkaline Aluminates.—Dr. K. J. Bayer.—The author has obtained a new aluminate of the formula $Al_2O_36Na_2O$.—(*Chemiker Zeitung*).

Oxalic Acid as a By-product of the Manufacture of Aniline.—Dr. R. Hirsch.—The acid which has served for the nitration of benzenes and toluenes contains from ½ to 1½ per cent of nitric acid. If allowed to stand for some time it deposits crystals of oxalic acid, formed at the expense of the carbide nitrated and of the *nitrous* acid. Hence it is necessary, in producing aniline, to use benzenes as free as possible from thiophenes, and nitric acid free from nitrous vapours.—(*Chemiker Zeitung*).

The Absorption of Reagents by Textile Fibres.—Dr. E. Knecht.—This memoir does not admit of useful abridgment.

Biedermann's Central-Blatt fur Agricultur Chemie.
Vol. xviii., No. 1.

Injuries in "Moor-Dam" Cultivation.—Prof. M. Fleischer.—A study of parasitic diseases encountered in the cultivation of reclaimed peat-lands.

Action of Ferrous Sulphate upon Different Soils.—P. Marguerite-Delacharlonny and L. Destremx.—An application of ferrous sulphate is beneficial if the iron oxide in the soil falls below 3·5 to 4 per cent, but useless or hurtful if the proportion is greater.

Manurial Value of Nitrogen in Soda Saltpetre and Sulphate of Ammonia as Applied to Potatoes.—Dr. Baessler.—On sandy soils the action of the sulphate of ammonia seems less certain than that of Chilian nitre as far as potatoes are concerned, but the experiments performed are not as yet decisive. For oats the two salts are equal.

Composition and Properties of the Peat of South Bohemia.—Prof. Farsky.—The author concludes that fibrous peat is a very advantageous litter for stables, &c., while peat siftings (turf-mull) is very useful as an addition to cess-pools.

Experiments at Rothamsted on the Growth of Turnips.—From the *Agricultural Student's Gazette.*

Experimental Field of the Danish Agricultural High School in 1860-1882 and 1883-1884.—P. S. Jörgensen and V. Maar.—The object of the experiments was to judge of the value of certain rotations of crops. In all the rotations the yield of barley was the smaller the larger the wheat harvest had been.

Researches on Smut, Mildew, and Canker in Grain.—J. L. Jensen.—The author criticises the means recommended for destroying the spores of these fungi in seed-corn. He finds that steeping for five minutes in water at 53° to 56° destroys the spores of the parasites without interfering with the germinating power of the grain.

Communications from the Laboratory of the Aylesbury Dairy Company.—Dr. P. Vieth.—In 1887 18,611 samples of milk were analysed and the sp. gr. of 80,000 samples was determined. The sp. gr. ranged generally from 1·030 to 1·034. The average total dry matter was 12·94 per cent, and the fat 3·82.

Application of the Reichert-Meissl-Wollny Analytical Process to Italian Butter and to Mixed Butters.—Professor C. Besana.—The melting-point in 114 samples of butter ranged from 33° C. to 37·7° C., and in one sample it reached 40·5° C. The proportion of volatile fatty acids in butter was found not to be constant. Differences were observed in butters made from the milk of the same set of cows at intervals of a few days. The quantity of decinormal alkali required for titrating the volatile fatty acids obtained from 5 grms. butter varied from 29 to 30·19 c.c. to 21·8 to 22 c.c., the latter figures being rare.

Zeitschrift fur Physikalische Chemie.
Vol. ii., Part 12.

Formation of Amide from Ester and Ammonia and the Inversion of this Reaction.—Albert Bonz.—The author's experiments confirm the incompleteness of the formation of amide from ester and ammonia, and explain it by the invertibility of the reaction; the limits of the condition of equilibrium of both reactions depend on the molecular weight, the temperature, and the relations of mass. The limits of the formation of esters rise with the increase of the molecular weight as well of the amide as of the alcohol.

Determination of the Basicity of Acids from the Electric Conductivity of their Sodium Salts.—W. Ostwald.—The author works out the principle that at corresponding degrees of dilution the conductivity increases proportionally to the basicity of the sodium salts. The particulars are given in a tabular form.

Outlines of a New Theory of Volume- and Refraction-Equivalents.—E. Ketteler.—This paper does not admit of useful abridgment.

The Molecular Volume of Sulphur.—H. Blitz.—This paper requires the two accompanying woodcuts.

The Kinetics of Bodies in Solution (Second Treatise).—Morris Loeb and Walther Nernst.—The authors find that the coefficient of temperature decreases with increasing mobility.

Apparatus for Determining the Depression of the Freezing-point.—J. F. Eykman.—The author gives his results in a tabular form.

Bulletin de la Société Chimique de Paris.
Vol. li., No. 2.

The Reduction of Copper Salts by Saccharine Matters.—L. Monnet.—The various sugars have the property of reducing the copper salts to the metallic condition if they are applied in concentrated solutions. In neutral liquids the reduction is produced at all temperatures, and heat merely facilitates the operation. The copper is always obtained in a crystalline condition. In alkaline solutions the reduction is effected only at a boiling heat, and the deposit is amorphous. Saccharose acts more easily than lactose or dextrose in neutral solutions; in alkaline liquids the reverse holds good.

Assay of Alcohols: Separation of the Aldehyds by Amines, and Especially by Metaphenylendiamine.—Ch. Girard and X. Rocques.—The authors dissolve in 200 c.c. of alcohol at 50° 3 grms. of metaphenylen-diamine hydrochlorate and boil for half an hour with an ascending condenser. The liquid takes a pale yellow colour. It is let cool for half an hour and slightly stirred towards the end of this time. The colour of the liquid darkens, and if aldehyd is present it takes a fine green fluorescence. It is then distilled quickly and 125 c.c. of distilled alcohol are collected, marking 75°. This is then submitted to Savalle's test and the tints obtained are compared with those given by alcohol at 75°, to which known quantities of pure amylic alcohol have been added.

On Hydrated Metallic Chlorides.—Paul Sabatier.—The stability of the hydrates examined agrees exactly with thermo-chemical indications.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 3.

A Novel Sophistication of Saffron.—M. Adrian.—The fraud consists in the addition of sodium borate, sulphate, and chloride, with potassium tartrate and ammonium nitrate together in the proportion of 43·75 per cent.

Determination of Oil of Mustard in the Seeds of Cruciferous Plants.—M. O. Foerster.—The author places in a retort 25 grms. of the substance previously pulverised and triturated with water. A current of steam is caused to traverse the retort and condense in a descending refrigerator, the end of which plunges for some centimetres below the surface of 50 c.c. of alcohol saturated with ammonia and placed in a ½-litre flask. The distillation is stopped when the volume of the condensed liquid amounts to 200 c.c. This liquid contains the thiosinnamine, and it is left for 12 hours in the stoppered flask. It is then heated in a beaker with an excess of mercuric oxide (freshly prepared by precipitating mercuric chloride with potassa), and heated, with constant stirring. Before cooling a sufficiency of potassium cyanide is added and the liquid is stirred until the precipitate of sulphur is freed from all foreign matters. It is then filtered, washed, dried, and weighed. The weight multiplied by 0·4266 gives the weight of thiosinnamine.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Water-Gas *v.* Coal-Gas.—Would some correspondent kindly inform me the relative amounts of carbonic acid gas evolved during combustion from water-gas and coal-gas, the former being represented by H_2CO, and the latter by the constituents of an ordinary coal-gas?—F. W.

Sulphate of Lime.—(1). In the case of a solution containing sulphate of lime in suspension which is the quickest way of separating same from the liquid? (2). After above is done, then the quickest and best way of condensing the liquid and obtaining crystallisation?—G. W.

MEETINGS FOR THE WEEK

MONDAY, 18th.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Wood Engraving," by W. J. Linton.
TUESDAY, 19th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
—— Society of Arts, 8. "Slavery in relation to Trade in Tropical Africa," by Commander V. Lovett Cameron.
WEDNESDAY, 20th.—Society of Arts, 8. "The Forth Bridge," by Benjamin Baker, M.Inst.C.E.
—— Meteorological, 7.
—— Geological, 8.
THURSDAY, 21st.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Chemical, 8. Ballot for the Election of Fellows.
—— Royal Society Club, 6 30.
—— Institute of Electrical Engineers, 8.
FRIDAY, 22nd.—Royal Institution, 9. "In the Heart of the Atlas," by Harold Crichton-Browne, F.R.G.S.
—— Quekett Club. (Anniversary).
SATURDAY, 23rd.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
—— Physical, 3. "Note on the Measurement of Electrical Resistance," by Dr. J. W. Waghorn. "Notes on Polarised Light," by Prof. S. P. Thompson. "On Electrical Measurements," by Prof. Ayrton, F.R.S., and Prof. J. Perry, F.R.S.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1526.

A METHOD OF VAPOUR DENSITY DETERMINATION.

By THEO. W. RICHARDS, of Harvard University, U.S.A.

In making some experiments upon the determination of the specific gravity of vapours, a method was recently stumbled upon which was apparently new, and which, when tried, gave excellent results; but, after the matter was wholly ready for publication, Professor Meyer called the writer's attention to the fact that methods based upon the same principle had already been published by Gibson Dyson,* and W. Bott and D. S. Macnair.† However, as the apparatus used in the present case differed in several respects from that heretofore used, and as the gentlemen mentioned above had apparently omitted an important correction from their calculation, it was deemed not wholly without purpose to publish the present investigation.

The method of determining the specific gravity of vapours which it is the object of this paper to describe is excessively simple. A cylindrical bulb and tubes of known volumes, with a dropping apparatus exactly like that described by Grünwald and Meyer‡ is attached to a barometer tube, while a water-pump is connected with the fine tube coming from the bottom of the bulb. After the latter is partially exhausted the pump is separated from the rest of the apparatus by a pinch-cock, and the bulb is heated to a constant known temperature. When the tension in the apparatus becomes also constant the height of the mercury supported is carefully noted.

The substance, which was placed in the drop apparatus before the exhaustion, is now allowed to fall into the heated bulb, and is vapourised; and the fall of the mercury column in the barometer indicates the tension of the vapour formed by the substance in filling the bulb of known volume at the known temperature.

Naturally the vapour remains at the bottom of the bulb in a much more concentrated condition than is indicated by this increase of tension, but the final effect is the same; and of course from the given weight, temperature, and volume, and the observed tension, the specific gravity of the vapour is easily deduced.

The underlying principle of this method, which it holds in common with those of Dyson, Bott, and Macnair, lies in the fact that here the pressure is the only variable, which it is the object of the experiment to observe. The fall of mercury will be the same with the same amount of a given substance, no matter what the tension of the residual air may have been. It will be noticed that the method is in no sense a modification of Victor Meyer's.

As before said, there is an important correction involved, which has apparently been heretofore omitted. The vapour as formed compresses the air in the bulb, and drives some of it up into the cold tube above; and of course this displaced air diminishes in volume on cooling, making the fall of the mercury less than it should be, and hence the specific gravity greater.

For this serious difficulty there are two methods of correction. The first is to determine by calculation first the amount of the air driven up (from the ratio of the air and vapour tensions as indicated by the barometer tube), then the amount of contraction of this volume in cooling from the higher temperature to the temperature of the room, and finally to find the influence of this contraction upon the fall of the mercury. The other method is experimental, and consists simply in sliding the bulb more deeply into the constant temperature bath, so that *just that volume* of air which was displaced into the tube will be heated to its previous temperature. This method is much simpler, and apparently is more reliable than the former.

The correction itself may be made much smaller than in the results published below, by diminishing the volume of the upper tubes, in an apparatus especially constructed for the purpose.

The apparatus may now be described more closely. The volume of the bulb and adjacent tubes was 189·2 c.c at 0° or 189·5 c.c. at 100 degrees, calculated, as usual, from its water capacity at a known temperature, and the coefficient of expansion of glass. To this value must be added 2·4 c.c., the average capacity of the connecting tube and upper part of the barometer tube to obtain the complete volume (191·9 c.c.) at 100°.

The bulb was surrounded by a vapour jacket closed at the top with a cork, through which passed its tubes and a wide air condenser. The total internal volume of the former, including the upper part of the barometer tube, was 15·3 c.c., and the cubic contents 0·33 c.c. for each centimetre of height.

The change of volume of the bulb, due to the elasticity of glass under pressure, is so small that it may be neglected.

The barometer tube was 2 m.m. in internal diameter. If it is much larger than this the fall of mercury will produce a sensible alteration in the volume, while, if it is much smaller, unequal capillarity will have too much effect on the readings. By rough measurement the capillary repulsion of this tube was found to be about 4·5 m.m.; of course this correction affects all readings equally, and must be applied only when we wish to compare them with an ordinary barometer. Naturally, the barometer tube must be clean, and of even diameter, and must be gently rapped before each reading. It was made of thick glass, and was clamped with the greatest rigidity, with its lower end in a large basin of mercury, whose level remains sensibly constant. The very slight error produced by the increase in volume, owing to the descent of the mercury (averaging 0·12 c.c.), might easily be corrected by the use of a cathetometer with two telescopes, and a deep vessel for mercury which could be raised or lowered; but it is so very slight that in practice it may be wholly neglected. In fact, it is quite sufficient to mark the mercury levels with a fine pencil upon labels pasted to the barometer tube, and to measure the distances between these marks with a centimetre rule, thus dispensing with a cathetometer altogether. All of the determinations given below were measured in this simple way.

The expansion of the mercury itself by the heat of the room may, of course, also be taken into account, but on so small a column it is less than the necessary experimental errors, and being in the opposite direction from the other infinitesimal corrections it may be, like them, neglected in practice. It must, of course, be considered when comparing with the outside pressure.

The method of conducting a determination is as follows:—After breaking off the end of the small sealed tube containing the substance, it is placed in the dropping apparatus. If we are dealing with a liquid it must contain no bubbles; if it is very volatile it may be necessary to surround the drop apparatus with a freezing mixture. The stopper is then applied, and the bulb is exhausted somewhat beyond the required point. The pump is then shut off by a pinch-cock, the height of the mercury marked, and the apparatus allowed to stand for some minutes as a test of air-tightness. When all is right the liquid of the bath is boiled, and, of course, the internal pressure of the apparatus rises, and the mercury falls, soon reaching constancy. This fall of mercury might, and probably will, be used, after suitable correction, as a

* Chemical News, lv., 88.
† *Berichte d. D. Ch. G.*, 1887, 916.
‡ *Ibid.*, xxi. (1888), 688.

method of determining the temperature, which must be known with some accuracy—otherwise the latter is determined by a thermometer in the vapour-bath.

When all has reached complete constancy, the tube containing the substance is allowed to drop into the bulb, and the increase of tension produced by its vapourisation is measured on the mercury column. The vapourisation is rapid, and after perfect constancy is once more attained the following calculation must be made:—As the total tension of the mixed air and vapour is to the tension of the vapour produced, so is the total volume of the tubes outside the bath to the volume of air driven up into them. This approximation, when divided by the capacity of the tubes per c.m., will give the number of c.m. which the bulb must be lowered into the bath, in order to correct for the cooling of the displaced air. After performing this operation, and waiting once more for constancy, which can be held for a long time, the fall of the mercury is carefully measured, and the whole apparatus is cleaned out by a stream of air and made ready for the next experiment. The whole operation does not last more than ten minutes, and is very easy in manipulation.

In the eight experiments which were tried, toluol was used as the test substance, and a steam-bath formed the source of heat. The first series of four was corrected by calculation; while the second series was corrected experimentally, and may be taken as a much better criterion of the method.

Density of Toluol Vapour.

First series, corrected by calculation.

T = 99·6°, Bar. = 749·5 m.m.

No. of experiment.	Weight. Grms.	Obs. fall. M.m.	Corr. fall. M.m.	Final tension. M.m.	Result.
1.	0·0333	42·10	42·94	225	3·24
2.	0·0216	27·85	28·40	118	3·18
3.	0·0430	53·63	54·70	332	3·28
4.	0·0195	24·40	24·90	82	3·27
				Average	3·242
				Theory	3·187

Second series, corrected experimentally.

T = 100°, Bar. = 760·9 m.m.

No. of experiment.	Weight. Grms.	Lowered bulb. C.m.	Corr. fall. M.m.	Final tension. M.m.	Result.
5.	0·0328	9·3	43·0	210·5	3·19
6.	0·0391	12·0	50·5	181·0	3·24
7.	0·0284	16·0	37·7	111·0	3·16
8.	0·0352	11·0	46·8	194·5	3·15
				Average	3·185
				Theory	3·187

The chief advantages of the method are its simplicity, the low tension and consequently low temperature required, the small amount of substance necessary, and the comparatively slight influence of impurity, the saving of time, and the complete absence of all mercurial or aqueous vapour. The chief disadvantage is that the temperature must be known with some exactitude, but it is probable, as before said, that the apparatus may itself form an air thermometer of just the degree of accuracy required.

In conclusion, the writer would once more express his warmest thanks to his friend Mr. W. P. Bradley for his interest and his assistance in the experimental work, and to Professor Victor Meyer for the use of his new laboratory.

Mention was omitted in a previous article* of papers by Dr. W. La Coste† and Dr. Schall.‡ These papers, which describe apparatus having the same end, but differing radically in principle and construction from that there described, were unknown to the author at the time of writing.

Göttingen, Jan. 18th, 1889.

* Chemical News, vol. lix., p. 39.
† *Berichte d. D. Ch. G.*, 1885, 2123.
‡ *Ibid.*, 1887, 1435, 1759, 1827, 2127.

SEPARATION OF ZINC AND NICKEL.

By H. BAUBIGNY.

The author has shown in a former paper that zinc may be completely precipitated by sulphuretted hydrogen from its saline solutions if they are dilute, and that if to the solution of a given weight of zinc sulphate we add sulphuric acid, the weight of the free acid necessary to overcome the action of the sulphuretted hydrogen decreases or increases with the volume of the solvent.

Since, for a given acid solution of zinc sulphate, the phenomenon varies with the degree of dilution, it seemed useful to ascertain if it would not be possible to effect the complete separation of this metal by fixing the liquid volume at what it ought to be for a weight of neutral salt containing a weight of acid equal to the sum of the free acid and of that in combination. Experiment verified the correctness of this principle.

It must be remarked, however, that the application of this fact becomes difficult, because the total precipitation of the zinc takes place so much the more slowly as the conditions of the medium differ from those obtained on setting out from the neutral, since the sulphide formed interferes in the action upon the undecomposed sulphate.

But if the weight of free acid is not greater than 5 to 6 times that in combination in the salt the method is applicable. Thus, 0·06 grm. of neutral sulphate, dissolved in 200 c.c. of water containing 0·27 grm. of SO_3 (= 9 times the weight of the acid in the salt) is completely decomposed in eight hours if the liquid is fully saturated with hydrogen sulphide. The water does not retain more than 0·0015 grm. of zinc sulphate.

As to acetic acid, if we add it to the solution of a neutral zinc salt it exerts no similar action. All takes place as in a neutral liquid, and even if the liquid of the solution contains from 20 to 25 per cent of actual acetic acid, all the zinc is thrown down by a current of sulphuretted hydrogen.

According to these observations, and to what the author has already established in the case of nickel and cobalt (*Comptes Rendus*, xciv., pp. 1183 and 1715; and cv., pp. 751 and 806), we have conditions which seem sufficient to permit the separation of zinc from these metals, and, *à fortiori*, ftom those which do not form sulphides in presence of water, such as aluminium and chromium, or less sulphurable, such as iron and manganese.

We have therefore to operate upon the acetic solution of the sulphates in the proportion of 0·3 grm. of the salts in 100 c.c. of liquid, treating them with a current of sulphuretted hydrogen.

In the case of zinc and nickel the mixed salts are dissolved in water containing 100 c.c. of glacial acid per litre, and the liquid treated at the common temperature with sulphuretted hydrogen is let stand two or three hours and then filtered. The deposit is then complete, and is perfectly white. The operation is completed by washing with water containing 10 per cent of acetic acid and containing sulphuretted hydrogen. The nickel is precipitated from the filtrate in the ordinary manner, raising the temperature to 70°—75°, and then letting it cool in presence of sulphuretted hydrogen in a stoppered flask. The free acid must be *exclusively* acetic acid, which is secured by adding to the liquid ammonium acetate. If we filter when the liquid is clear and cold all the nickel is separated as a dense sulphide, which is washed with water charged with sulphuretted hydrogen

and acidulated with one or two per cent of acetic acid. The sulphides are then converted into sulphates and weighed after drying at 400°.

Experiment proves that if the mixed sulphates contain little nickel, one-third at most, the addition of acetic acid is useless.—*Comptes Rendus* (vol. cviii., p. 236).

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 82).

Method for the Analysis of Cattle Food.

Hygroscopic Moisture.—Dry 2 to 3 grms. at 100° C. to constant weight.

Ash.—Char the substance at a low red heat, exhaust the charred mass with water, burn the insoluble residue, add the ash to the residue from the evaporation of the aqueous extract obtained above, dry the whole at 110°, and weigh. Determine carbonic acid and insoluble matter (sand and charcoal) in the product for the estimation of the pure ash.

Ether Extract.—Pulverise the air-dry substance till all of it will pass through a sieve with less than one-sixtieth inch mesh; dry about 5 grms. at 100°, and take about 2 grms. for each extraction. Exhaust with anhydrous ether of specific gravity 0·720 to 0·725, not less than eight hours continuously. Dry ether extract at 100° in a current of dry hydrogen to a constant weight.

Crude Protein.—Determine nitrogen by the Kjeldahl method in the manner recommended by the Nitrogen Committee, and multiply the result by 6·25 for the crude protein.

Albumenoid Nitrogen, Stutzer's Method.—Prepare cupric hydrate as follows:—Dissolve 100 grms. of pure cupric sulphate in 5 litres of water and add 2·5 c.c. of glycerin; add dilute solution of sodium hydrate till the *liquid* is alkaline; filter, rub the precipitate up with water containing 5 c.c. of glycerin per litre, and then wash by decantation or filtration till the washings are no longer alkaline. Then rub the precipitate up again in a mortar with water containing 10 per cent of glycerin, thus preparing a uniform gelatinous mass that can be measured out with a pipette. Determine the quantity of cupric hydrate per 1 c.c. of this mixture.

To 1 grm. of the substance, pulverised as for the determination of the ether extract, add 100 c.c. of water in a beaker, heat to boiling, or in case of substances rich in starch heat on the water-bath ten minutes, add a quantity of the cupric hydrate mixture containing 0·7 to 0·8 grm. of the hydrate, stir thoroughly, filter when cold, wash with cold water, and without drying put the filter and its contents into the concentrated sulphuric acid for the determination of the nitrogen after Kjeldahl. For filtering use either Schleicher and Schull's No. 589 filter paper or Swedish paper, either of which contains so little nitrogen that it can be left out of account.

If the substance examined consists of seed of any kind or residues of seeds, such as oil-cake or anything rich in alkaline phosphate, add a few c.c. of a concentrated solution of alum just before adding the cupric hydrate, and mix well by stirring. This serves to decompose the alkaline phosphate, precipitating aluminum phosphate; if this is not done cupric phosphate and pure alkali may be formed, and the protein copper may be partially dissolved in this alkaline liquid.

Crude Fibre, Weende Method.—Pulverise as for the ether extract, and extract the fat, at least nearly completely. To 2 grms. of the substance in an Erlenmeyer flask add 200 c.c. of boiling 1·25 per cent sulphuric acid, boil immediately and for thirty minutes continuously with as much rotary motion as may be necessary to keep all the substances that may tend to adhere to the sides of the flask in contact with the liquid, throw on a filter of finest linen, and rinse the flask and wash the contents of the filter thoroughly with boiling water. Wash the contents of the filter back into the flask with 200 c.c. of a 1·25 per cent solution of sodium hydrate, at once raise to boiling, and boil continuously for thirty minutes with rotary motion as above described, filter through a Gooch crucible or according to some similar device, and wash very thoroughly with boiling water. Such thorough washing has been found to be essential to success. Wash then with alcohol and finally with ether, dry at 100°, weigh, incinerate, and give the loss of weight for crude fibre.

Statement of Results.

	In the substance in its natural condition (or as received).	In the dry substance.
Moisture		
Crude ash		
Ether extract		
Crude fibre..		
Crude protein		
Nitrogen: Total ..		
Albumenoid..		

(To be continued).

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

RE-CALCULATIONS OF THE ATOMIC WEIGHTS.*

By F. P. VENABLE.

(Concluded from p. 79).

Methods of Calculation.

Clarke, Sebelien, and others, who have worked over this problem, have been greatly troubled as to what data should be used in the re-calculations and what rejected. Manifestly the results of many of the older experimenters can lay no great claims to accuracy. Some, as Clarke says, are "chemically worthless because of constant errors." Many have neglected proper precautions or necessary corrections. And yet there are reasons for retaining much of this, and the retention or rejection is a point of judgment on which chemists may, and do, legitimately differ. An additional sentence of Clarke's reveals the extent of the trouble. "In fact it is doubtful," he says, "whether any two chemists, working independently, would handle all the data in precisely the same way, or combine them so as to produce exactly the same final results."

The accompanying tables, giving the calculations of Clarke, Meyer and Seubert (the O=16 table was worked out from their O=1), Van der Plaats, and Ostwald,† show the truth of this. The two last agree more nearly than the others, and yet the variations are numerous and sometimes as large as 5 in the case of osmium; 3 in the case of mercury; 1 in the case of uranium, &c. Unanimity in regard to an atomic weight does not always mean that the weight is correct. Paucity of data sometimes limits the chances for variation. Indium, for instance, and gallium and beryllium have been subjected to few investigations.

The mathematical side of the question, whether the method of least squares should be adopted, or by what

* From the *Journal of the Elisha Mitchell Scientific Society*, Vol. v., Part 2.

† Ostwald's table is put down under the head of O=16. He gives it as H=1 and also O=16, but the numbers most nearly correspond with the latter.

TABLE No. II.

Oxygen = 16.

Symbol.	Clarke.	Meyer and Seubert.	Van der Plaats.	Ostwald.
Ag	107·923	107·929	107·93	107·938
Al	27·075	27·107	27·08	27·08
As	75·090	75·087	75·0	75·0
Au	196·606	196·690	196·7	196·7
B	10·966	10·927	11·0	11·0
Ba	137·007	137·202	137·1	137·04
Be	9·106	9·103	9·1	9·10
Bi	208·001	208·019	208 0	208·01
Br	79·951	79·954	79·955	79·963
C	12·0011	11·999	12·005	12·000
Ca	40·082	40·009	40·0	40·00
Cd	112·092	111·979	112·1	112·08
Ce	140·747	141·553	141·5	141·5
Cl	35·451	35·458	35·456	35·453
Co	59·023	58·746	58·8 or 60	59·1
Cr	52·127	52·581	52·3	52·3
Cs	132·918	133·032	132·8	132·88
Cu	63·318	63·338	63·33	63·33
Di	144·906	145·362	145·0	145·0
Er	166·273	166·415	166·0	166·0
F	19·027	19·109	19·0	19·01
Fe	56·042	56·015	56·0	56·00
Ga	68·963	70·072	70·0	69·9
Ge	72·32	= Determination of Winkler.		
H	1·0023	1·0024	1·00	1·00
Hg	200·171	200·299	200·1	200·4
I	126·848	126·856	126·86	126·864
In	113·659	113·683	113·7	113·7
Ir	193·094	192·981	193·0	193·11
K	39·109	39·128	39·144	39·136
La	138·844	138·846	138·0	138·5
Li	7·0235	7·028	7·02	7·030
Mg	24·014	23·999	24·4	24·38
Mn	54·029	54·937	55·0	55·02
Mo	95·747	96·139	96·0	95·9
N	14·029	14·045	14·05	14·041
Na	23·051	23·052	23·05	23·058
Nb	94·027	93·934	9·40	94·2
Ni	58·062	58·746	58·0 or 58·8	58·5
O	16·000	16·000	16·000	16·00
Os	198·951	195·487	195·0	200·0
P	31·029	31·037	30·95	31·03
Pb	206·946	206·906	206·91	206·911
Pd	105·981	106·465	106·5	106·0
Pt	194·867	194·826	194·9	194·83
Rb	85·529	85·413	85·4	85·44
Rh	104·285	104·360	104·0	103·05
Ru	104·457	103·759	104·0	103·8
S	32·058	32·059	32·06	32·063
Sb	120·231	119·899	120·0	120·29
Sc	44·081	44·079	44·0	44·09
Se	78·978	79·067	79·0	79·07
Si	28·260	28·07	28·0	28·06
Sm	—	—	150·0	150·2
Sn	117·968	117·643	118·1	118·12
Sr	87·575	87·518	87·5	87·52
Ta	182·562	182·455	182·8	182·8
Te	128·254	128·019	125·0	125·2
Th	233·951	232·539	233·0	233·0
Ti	49·961	50·373	48·1	48·12
Tl	204·183	204·209	204·2	204·146
U	239·030	240·399	240·0	239 0
V	51·373	51·228	51·3	51·21
W	184·032	184·059	184·0	184·0
Y	90·023	89·824	89·5	89·0
Yb	173·158	173·081	173·0	173·2
Zn	65·054	65·042	65·3	65·38
Zr	89·573	90·626	90·5	90·7

Hydrogen = 1.

Symbol.	Clarke.	Meyer and Seubert.
Ag	107·675	107·66
Al	27·009	27·04
As	74·918	74·9
Au	196·155	196·2
B	10·941	10·9
Ba	136·763	136·86
Be	9·085	9·08
Bi	207·523	207·5
Br	79·768	79·76
C	11·9736	11·97
Ca	39·990	39·91
Cd	111·835	111·7
Ce	140·424	141·2
Cl	35·370	35·37
Co	58·887	58·6
Cr	52·009	52·45
Cs	132·583	132·7
Cu	63·173	63·18
Di	144·573	145·0
Er	165·891	166·0
F	18·984	19·06
Fe	55·913	55·88
Ga	68·854	69·9
Ge	—	—
H	1·0000	1·00
Hg	199·712	199·8
I	113·398	113·4
In	113·398	113·4
Ir	192·651	192·5
K	39·019	39·03
La	138·526	138·5
Li	7·007	7·01
Mg	23·959	23·94
Mn	53·906	54·8
Mo	95·527	95·9
N	14·021	14·01
Na	22·998	22·995
Nb	93·812	93·7
Ni	57·928	58·6
O	15·963	15·96
Os	198·494	195·0
P	30·958	30·96
Pb	206·471	206·39
Pd	105·737	106·2
Pt	194·415	194·34
Rb	85·251	85·2
Rh	104·055	104·1
Ru	104·217	103·5
S	31·984	31·98
Sb	119·955	119·6
Sc	43·980	43·97
Se	78·797	78·87
Si	28·195	28·0
Sm	—	—
Sn	117·698	117·35
Sr	87·374	87·3
Ta	182·144	182·0
Te	127·960	127·7
Th	233·414	231 96
Ti	49·846	50·25
Tl	203·715	203·7
U	238·482	239·8
V	51·256	51·1
W	183·610	183·6
Y	89·816	89·6
Yb	172·761	172·0
Zn	64·9045	64·88
Zr	89·367	90·4

formulæ the probable errors should be calculated, and by what the results combined, is of course of great importance and the subject of varying views, but cannot be discussed here.

Out of 66 elements the revisers agree on 29 to the tenth place of decimals, differing in the hundredth place only. In the remaining 37 or 56 per cent the differences are more or less great.

The increased interest in these re-determinations of atomic weights, giving fresh data for calculation and enabling us to throw off some of the burden of faulty determinations, gives promise of an approximately correct table in the near future.

I cannot close without adverting to the speculations of some authors as to the question whether we are to expect these atomic weights to be fixed quantities. In other words,

Are the Atomic Weights Constant?

This question Stas proposed to himself before starting upon his classic work on the atomic weights. The conclusion he drew from his experiments was that they were unchangeable. The question has been raised again by Schützenberger and Butlerow.* Butlerow does not doubt the results obtained by Stas, but suggests that under changed conditions or with different bodies the results might have been otherwise.

Of course if the atomic weights are not constant the law of constant proportions is without support and must be given up, and this would necessitate a revolution in chemistry as a science.

These authors suppose the range of variation in the weights to be very slight, yet distinctly to be detected by analysis. The theories of both are supported by analytical data, in which the authors seem to place the utmost confidence. If their results are not accurate the variability of the atomic weights stands unproven. To show the nature of their experiments, Sebelien quotes from Schützenberger's work his synthesis of water. According as this is carried out with copper oxide at red heat, or by the lowest possible temperature, or with lead chromate, the relation between the oxygen and hydrogen varies from 7·89 to 7·98. Or again, the atomic weight of iron, determined from the nitrate, he finds to be 54, whilst that from the oxalate is 56. He found also that carbon dioxide prepared by burning pure carbon at a high temperature contained more oxygen than that prepared by means of carbon monoxide from organic bodies.

The generality of chemists will be more apt, I think, to suppose the analytical work of these investigators faulty than to accept their conclusions as to the inconstancy of the atomic weights. Yet the matter is of the utmost importance and should be decided with as great freedom from preconceived notions as possible. It is a question exceedingly difficult to decide, and will require great nicety and accuracy of work. Many of the most trusted leaders of work and thought in the science will have to concur in testimony derived from their own experiments before any attempt at altering the science to suit the new facts will be made.

We must not say, because we are mentally satisfied with the present theories, and dread the trouble which so radical a change would cause, that the supposition is impossible and need not be considered.

Butlerow offers three possible explanations of his own and Schützenberger's observations:—

1. The absolute amount of matter has been increased in that the so-called force or energy has been changed into matter.

2. The absolute amount of matter is unchanged, but its weight is increased by means of a temporary increase in the intensity with which the earth attracts matter.

3. The weight of matter is not increased in either way, but the chemical value is changed. The atomic weight of carbon, for instance, may be temporarily changed from 12 to 11·8, and thus the saturation capacity of carbon raised by about $\frac{1}{60}$. The amount of carbonic acid made from the same amount of carbon would thus be increased and would be richer in oxygen.

The first two suppositions would be subversive of Natural Philosophy generally. The last would simply be subversive of chemistry as now systematised. As Sebelien says, we must give up under the third supposition our idea of atoms, for an atom is nothing if not a fixed weight of something. Vogel* has also come to the conclusion that the atomic weights vary because those got by the use of certain compounds differ throughout from those derived from other compounds. By this assumption he also explains the cases in which analyses result in a sum total of over 100 per cent. It seems much more plausible to explain these variations on the ground of errors of analysis, constant errors of method, impurities of materials, and the many other difficulties and obstacles which a chemist meets in such work, than by the radical assumption of an inconstancy in the very constants on which the science is founded and built up.

At any rate, until much more proof is forthcoming, the matter must rest in abeyance.

* *Bull. de la Soc. Chim. de Paris*, xxxix., 258. *Ibid.*, xxxix, 263 (cited in *Zeitschrift fur Anal. Chemie*, xxii., 640, and Sebelien, "Geschichte der Atomgewichte," 54.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1888.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, February 7th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The results furnished by the examinations of the water supplied to the Metropolis, made daily during the month of January, are extremely good, and indeed exceptionally good for the period of the year. Thus, in the case of the Thames-derived waters, for example, the mean proportion of organic carbon was found to be only 0·170 part in 100,000 parts of the water, with a maximum in any one sample examined of 0·197 part; this maximum result for January, 1889, being almost identical with the mean result, or 0·196 part, for the previous month of December, 1888. That this last mean result was not at all excessive for the period of the year may be gathered from the consideration that even a proportion of 0·280 part of organic carbon in 100,000 parts of the water corresponds as nearly as may be to about half a grain only of organic matter per gallon. Of the 189 samples of water examined, two of the

* *Nature*, vol. xli., p. 42.

Thames-derived samples were alone recorded as exhibiting a very slight turbidity.

We are, Sir,

Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. Albert Cooper, W. Hepworth Dixon, F. C. Garrett, F. B. Guthrie, John Percival, and R. W. Woosnam were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. T. D. Collis, Barry, Asirgarh, Central India; Harry Broadbent, 31, Victoria Terrace, Belle Vue Road, Leeds; Edward Barnwell Cook, Clifton College, Bristol; Francis Edward John Cridland, Mayfield, Southboro, Surbiton; Alexander Archie Cunningham, American Sugar Refinery, Battery Street, San Francisco, U.S.A.; Thomas Hill Easterfield, Clare College, Cambridge; Joseph T. Freestone, 33, Brownlow Road, New Ferry, Cheshire; Richard Ashworth Hoyle, 11, Market Square, Lytham; Herbert Ingle, Poole, near Leeds; Christopher J. McNally, M.D., Medical College, Madras; William Beattie Nesbitt, University of Toronto; Charles Proctor, 192, Barry Road, Dulwich, S.E.; Arthur Avery Read, Owens College, Manchester; Ernest Reckitt, Caen Wood Towers, Highgate, N.; Henry Charles Anslie Vine, 15, Old Pond Street, Bath; Walter Arthur Voss, Oak House, Croydon Road, Anerley; John Tsawoo White, Rangoon College, Rangoon.

The following papers were read:—

11. "*Researches on the Constitution of Azo- and Diazo-derivatives. V. Compounds of the Naphthalene-β-series*" (*continued*). By R. Meldola, F.R.S., and G. T. Morgan.

The authors describe the preparation of benzoyl-derivatives of azo-β-naphthol compounds by the displacement of the amido-group in the corresponding amido-derivatives by $C_7H_5O{\cdot}O$—by means of the diazo-interaction in the presence of benzoic acid. The method is analogous to that described last year by one of the authors and F. J. East (*Berichte*, 1888, 601; *Chem. Soc. Trans.*, 1888, 465) for the preparation of azophenylic acetates, action takes place in accordance with the equation—

$$R{\cdot}N_2{\cdot}OH + HO{\cdot}C_7H_5O = R{\cdot}OC_7H_5O + N_2 + H_2O.$$

The *metanitrobenzeneazobenzoate*,—

$$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O(\beta),$$

has been prepared by the foregoing method, as well as by the direct benzoylation of metanitrobenzeneazo-β-naphthol by means of dry sodium benzoate and benzoyl chloride; it crystallises in orange needles melting at 171°. Benzeneazo-β-naphthol, when similarly treated with benzoyl chloride and sodium benzoate, gives *benzeneazo-β-naphthyl benzoate*, $C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OC_7H_5O$, which crystallises in dense orange prisms melting at 125°. The greater portion of the paper is devoted to a study of the products of reduction of the azo β-naphthol-derivatives containing acid radicles. When violently reduced with tin and chlorhydric acid, benzeneazo-β-naphthol acetate yields aniline and α-amido-β-naphthol, mixed with a small quantity of a monacetyl-derivative of the base diamidohydroxynaphthyl-phenyl,—

$$NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH\beta)(NH_2\alpha),$$

the acetyl-group being most probably present in the α-amido-group in consequence of intramolecular transference in the ortho-position (Böttcher, *Berichte*, 1883, 1933). The triacetyl-derivative of the hydroxynaphthyl-phenyl base crystallises in white needles melting at 252°. If benzeneazo-β-naphthyl acetate be reduced in cold alcoholic solution with stannous chloride the monacetyl-derivative of the hydroxynaphthyl-phenyl base is the chief product; but the instability of this compound does not allow of its being isolated. In a similar manner, it has been found that when boiled with tin and chlorhydric acid in alcoholic solution, benzeneazo-β-naphthyl benzoate gives aniline and α-amido-β-naphthol, the benzoyl being split off. α-Amido-β-naphthol and aniline are the chief products of mild reduction with stannous chloride, but the monobenzoyl-derivative of the naphthyl-phenyl base is also formed; the latter crystallises in white needles melting at 172—173°: the authors assign to it the formula $NH_2{\cdot}C_6H_4{\cdot}C_{10}H_5(OH\beta)(NH{\cdot}Bz\alpha)$, and suppose that the benzoyl is transferred to the amido-group as before by the intermediate formation of the anhydro-base. The diacetyl- and dibenzoyl-derivatives of α-amido-β-naphthol, $C_{10}H_6\langle^{NH{\cdot}C_2H_3O(\alpha)}_{O{\cdot}C_2H_3O(\beta)}$, and $C_{10}H_6\langle^{NH{\cdot}C_7H_5O(\alpha)}_{O{\cdot}C_7H_5O(\beta)}$, are also described. The first crystallises in colourless rhombic prisms melting at 206°, and the second in whitish needles melting at 226·5°. The authors are engaged in investigating the products of reduction of the alkyl-derivatives of azo-β-naphthol compounds.

12. "*The Action of Nitric Acid on Anthracene.*" By A. G. Perkin.

Experiments on the preparation of nitro-derivatives of anthracene have up to the present failed, owing to the fact that when anthracene is treated with nitric acid oxidation and nitration take place simultaneously, the products being anthraquinone and nitroanthraquinones. Nitro-derivatives of anthracene may, however, readily be prepared, provided that during the interaction of the anthracene and the nitric acid care is taken at once to decompose any nitrous acid which may be formed. If anthracene be gradually added to strong nitric acid (which has been carefully freed from nitrous compound by boiling it with urea), it is quickly converted into a new yellow substance, which after re-crystallisation from coal-tar naphtha proved on analysis to be *dinitroanthracene*. This may also be prepared by the addition of anthracene to nitric acid diluted with nitrobenzene or the nitrates of the pyridine bases.

Dinitroanthracene crystallises in long, brilliant, yellow needles, which are difficultly soluble in the ordinary solvents. When carefully heated in a test-tube, it sublimes apparently without decomposition, but on long heating it is converted quantitatively into anthraquinone, with evolution of nitrous fumes, a proof that its constitution is represented by the formula $C_6H_4{\cdot}C_2(NO_2)_2{\cdot}C_6H_4$. The same change takes place when dinitroanthracene is oxidised with chromic acid, and also when it is exposed for some weeks to the action of sunlight.

Mononitroanthracene is contained, together with anthraquinone, in the mother-liquors from the preparation of dinitroanthracene. It crystallises from naphtha in small yellow needles, which are more readily soluble in this solvent than dinitroanthracene, but not so soluble as anthraquinone.

Diamidoanthracene is readily obtained by adding dinitroanthracene to a boiling solution of sodium sulphide in alcohol, and precipitating the resulting violet solution with chlorhydric acid. The orange powder thus produced is dissolved in hot alcohol, a little potash is added, and the solution allowed to cool. In this way beautiful silky, orange needles are obtained, which on analysis give numbers agreeing with those required for the formula $C_{14}H_8(NH_2)_2$. Diamidoanthracene is readily soluble in benzene and carbon bisulphide, less soluble in alcohol

It melts at 146°, and on oxidation with chromic acid yields anthraquinone.

The author is engaged in the further investigation of these substances.

13 "*The Preparation of Glyceric Acid.*" By T. Lewkowitsch, Ph.D.

Debus (*Annalen*, cvi., 79) and Sokoloff (*Annalen*, cvi., 85) recommend preparing glyceric acid from its repeatedly re-crystallised calcium salt by means of the requisite quantity of oxalic acid; Mulder (*Ber.*, xiii., 1902), however, has proposed the use of lead glycerate and its treatment with sulphuretted hydrogen.

When recently preparing a quantity of glyceric acid, the author has found that it is impossible to completely convert the lead salt in the way indicated by Mulder, part of the lead remaining dissolved. A great number of experiments, carried out under various conditions, led all to the same result.

It is therefore necessary to return to the old prescription of Debus and Sokoloff, viz., to prepare glyceric acid from its calcium salt by means of oxalic acid.

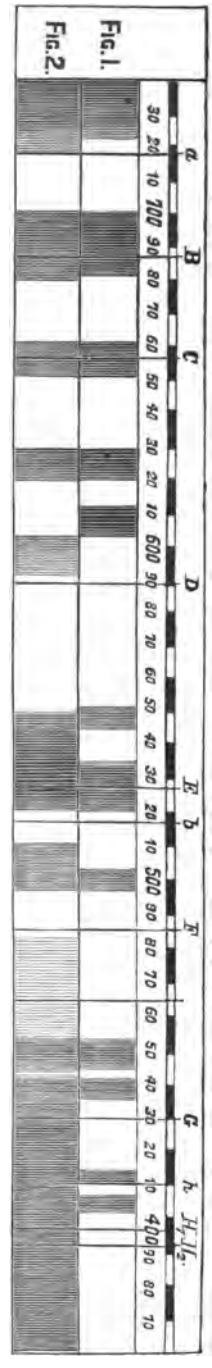
14. "*The Relation of Cobalt to Iron as Indicated by Absorption-spectra.*" By W. J. Russell, Ph.D., and W. J. Orsman, Junr.

It is well known that when examined spectroscopically, some coloured metallic compounds are found only to produce a general absorption, but from previous observations it seemed possible to the authors that in some cases at least this might be resolved into bands by employing more powerful chemical agents than are generally used in such cases; experience had indicated that the chloride is usually the most suitable salt, and that it should be dissolved in chlorhydric acid and the liquid saturated with hydrogen chloride, also that, if possible, ether should be taken as solvent.

Applying these views to iron, it was found that ferric chloride gave a banded spectrum strikingly similar to that of cobalt chloride. Irons of all kinds were examined: pig iron, commercial cast iron, and various manufactured articles; steel in the form of wire, needles, and knives; and a number of specimens of reputed pure iron, viz., Demidorff's sheet iron, a sample of which was kindly given to the authors by Mr. Crookes, electro-deposited iron, and some ancient Indian iron from Professor Roberts-Austen, and iron prepared by the late Dr. Matthiessen. Also a large number of iron ores—hæmatite Elba ore, Welsh bog ore, micaceous ore, ordinary spathic ore, a spathic ore found in cryolite, for which the authors have to thank Dr. Müller; Siderite, pyrites from the chalk, wolfram and rouge. Iron was also separated from the ignited residue of blood. All the specimens examined gave the same result.

Fig. 1 represents the bands seen in a solution of cobalt chloride to a scale of wave-lengths; the three most refrangible bands are easily photographed, but are not visible to the eye under ordinary conditions. The iron spectrum (Fig. 2) in general appearance closely resembles the cobalt spectrum, but the band which in cobalt is at 605 is slightly shifted nearer the blue, as shown in the diagram; there appears also to be a shift in the 501 band, but in the opposite direction. It was found that ether always dissolved out of the ferric chloride a substance which gave a band of extraordinary intensity, exactly agreeing in position with the 530 band in the cobalt spectrum; further, that on increasing the strength of the ethereal solution, other bands became visible, agreeing with the bands observed in the strong chlorhydric solution of ferric chloride, and differing only in the case of the 690 and 655 bands, which in the ethereal solution were nearer the blue. Fig. 2 is the spectrum observed in a solution of iron in chlorhydric acid, peroxidised by any ordinary means.

For a variety of reasons the authors believe that this spectrum (Fig. 2) does not arise from the presence of cobalt in the iron. In the first place there is a constant



difference between the two spectra, as shown in the position and appearance of the band at 597. A trace of cobalt dissolved along with the iron gives the same spectrum as pute cobalt dissolved in chlorhydric acid. Again, on gradually increasing the strength of a pure cobalt chloride solution, the bands in the red are the first to appear, and the band at 530 is not visible until the general absorption has crept up as far as 580, completely blocking up the red end of the spectrum; in an ethereal

solution from iron, on the contrary, this 530 band is the first to appear, and the bands in the red only become visible in comparatively strong solutions. Ether extracts the band-giving substance from the ferric chloride with great ease; but it abstracts nothing from the cobalt chloride. Again, on dissolving iron in chlorhydric acid, no bands are visible, and so long as the iron is in the ferrous state, even ether extracts no band-giving substance; but on converting the ferrous into ferric chloride by nitric acid or potassium chlorate, &c., the band-yielding substance is at once apparent. A known weight of Mr. Crookes's Demidorff iron was converted into chloride and dissolved in a known volume of ether, and the intensity of the bands, compared with those given by cobalt chloride dissolved in a similar bulk of chlorhydric acid; it was found that approximately it required a weight of cobalt equal to that of the iron to give bands of similar intensity.

DISCUSSION.

Mr. J. NORMAN LOCKYER said that some years since, in a paper communicated to the Royal Society, he had suggested that there were many different molecular groupings of the same element possible, and that spectrum analysis would disclose these; if the same molecular grouping were demonstrated in several substances, then undoubtedly there was a common constituent. If the bands described by the authors represent a substance common to iron and cobalt, it should be possible to obtain spectroscopic evidence of its presence at some temperature on volatilising the metals; although he had not fully studied cobalt and nickel comparatively, he had, in fact, found that under certain special conditions some of the spectroscopic appearances were common to both, and in such a marked degree as to render it improbable that they were caused by impurities.

Dr. PERKIN referred to the non-appearance of bands in an alcoholic solution of purpurin and their appearance in an ethereal solution, as an illustration of the influence of the solvent.

Dr. ARMSTRONG remarked that the slight shift of the bands which had been referred to did not necessarily indicate that different substances were primarily the cause of the absorptions, as it was well known that such effects were observed on employing different solvents; the absorbing substance might, in the one case, be held in combination more firmly than in the other; this view was in harmony with the statement that ether did not extract the band-yielding substance in all cases.

Dr. RUSSELL, in reply, said that not the spectrum as a whole, but only one of the bands, was shifted. His view was that the solvents had broken up the substance into a finer state.

15. "*Note on Methyl Fluoride*," By NORMAN COLLIE, Ph.D.

MM. Moissan and Meslans have recently described (*Comp. Rend.*, Dec. 31, 1888) a new method of preparing methyl fluoride; but they do not seem to be aware that this substance had already been obtained in a state of purity (Lawson and Collie, *Chem. Soc. Trans.*, 1888, 626); the opportunity is therefore now taken to describe further experiments made with the gas.

The measurements of some of the physical constants of methyl fluoride have been made in conjunction with Professor Ramsay. The vapour pressures, taken at temperatures varying from −5° C. to 45° C. are as follows:—

Temp.	Press.	Temp.	Press.	Temp.	Press.
	M.m.		M.m.		M.m.
−5° C.	11365	15° C.	23003	35° C.	36204
0	14696	20	25621	40	40496
5	17740	25	28840	45	46010
10	20091	30	32756	—	—

The substance assumes the critical state at 44·9° C. and at a pressure of 47123 m.m. This pressure is probably slightly too high, owing to a trace of air, and the temperature too low. The error in pressure probably does not exceed 1500 m.m., and of temperature 0·2° C.

A determination of the relative density of the gas gave 17·38, the theoretical number being 17·05. On exposing a mixture of equal volumes of methyl fluoride and chlorine to sunlight, it became colourless in a few hours, the interaction being $CH_3F+Cl_2 = CH_2ClF + HCl$. The further action of chlorine was found to take place much more slowly, and attempts to prepare CCl_3F were without success.

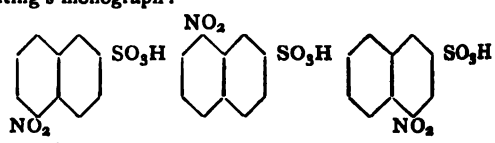
DISCUSSION.

Professor THORPE, after remarking on the importance of Moissan's researches on fluorine and its compounds, said that he feared that our Continental colleagues were less prone to take note of our work than we were of theirs. Moissan was generally said to be the discoverer of phosphorus trifluoride and oxyfluoride, but as a matter of strict history the former was first described by J. MacIvor, in the CHEMICAL NEWS (1875, xxxii., 232), and the latter by Schulze (*J. Pr. Chem.*, 1880, xxi., 442).

Dr. COLLIE said that he had incidentally described the preparation of methyl fluoride in a paper on the action of heat on tetramethylammonium compounds, and it was therefore not remarkable that his method had remained unnoticed by Moissan.

16. "*The Nitration of Naphthalene-β-Sulphonic Acid.*" By HENRY E. ARMSTRONG and W. P. WYNNE.

According to Cleve, *three* isomeric α-nitro-β-sulphonic acids are produced on nitrating naphthalene-β-sulphonic acid; the chlorides of these acids melt respectively at 169°, 140°, and 125°. The sulphochloride melting at 125° corresponds to η-dichloronaphthalene (m. p. 48°); the remaining two were originally supposed by Cleve to furnish one and the same dichloronaphthalene melting at 61°, but subsequently he considered it probable that two distinct dichloronaphthalenes were formed, which melted at the same temperature, and this conclusion would appear to receive support from the authors' discovery that there are two which melt at nearly the same temperature, viz., 1 : 3 $C_{10}H_6Cl_2$ (m. p. 61·5°) and 1 : 2' or 1 : 3' $C_{10}H_6Cl_2$ (m. p. 63·5°). In a recent paper (*Ber.*, 1888, 3275) Cleve has provisionally represented the three acids in question by the following formulæ, which had, however, previously been made known in Reverdin and Nölting's monograph:—



Sulphochloride: M. p. 125°. M. p. 140°. M. p. 169°.

A variety of considerations have led the authors to attempt the preparation of these acids: in the first instance they became specially interested in them on account of the supposed occurrence of isomeric change on treating two of them with PCl_5; then, when it was discovered that two dichloronaphthalenes existed which melted at nearly the same temperature, corresponding, it was to be presumed, to two of the acids, it became of importance to ascertain which of the acids corresponded to the one and which to the other dichloronaphthalene, as their constitution would thereby be determined; and lastly because, in the event of one of the acids being found to yield 1 : 3 dichloronaphthalene, the direct production of meta-derivatives of naphthalene would be established, a result of considerable theoretical importance, inasmuch as hitherto it has always been found that a heteronucleal α-derivative is formed in cases in which the corresponding benzene-derivative would afford a meta-derivative.

The authors have nitrated potassium naphthalene-β-sulphonate by grinding it up with 2·5 mol. proportions of nitric acid (1·5), and then heating on the water-bath; as soon as dissolution was effected, water was added, and

the solution evaporated on the water-bath, water being frequently added. A partial separation of the isomeric acids by means of the barium salts was first effected in the manner recommended by Cleve; the various fractions were subsequently treated with PCl_5, and the sulphochlorides crystallised alternately from benzene, acetic acid, and carbon bisulphide. It was found that the nitration was complete. Both on account of the large proportion of the chloride melting at 169° which is obtained, and of its high melting-point, the authors were led to expect that this compound would prove to correspond to the heteronucleal dichloronaphthalene melting at 63·5°, rather than to the 1 : 3-derivative, as indicated by Cleve's formula, and they actually find this to be the case; on heating the sulphochloride with PCl_5 at 220°, then steam distilling, re-steaming the product, and crystallising it from alcohol, a dichloronaphthalene was obtained which melted at 62·5 to 63°; the sulphonic acid prepared therefrom gave an anhydrous potassium salt and a sulphochloride which, soon after its separation, when only partially opaque, melted at 115°, but subsequently, when entirely opaque, at 117·5°. Cleve's two nitrosulphochlorides, melting at 125° and 169°, therefore correspond respectively to the Dahl and Badische modifications of beta-naphthylamine sulphonic acid.

All attempts to separate a third sulphochloride have been unattended with success: products of intermediate melting-point have indeed been obtained, but on recrystallisation have been resolved into the two chlorides melting at 125° and 169°. This result is perhaps significant, if the theoretical improbability of the formation of a meta-compound be borne in mind; but the authors are loth to accept the apparently logical interpretation of their results, as they are unacquainted with the precise conditions under which Cleve worked—only a very brief statement of his method having been made public—especially as the third acid is said by Cleve to be sparingly produced, and as it is within their own experience that slight variations in treatment, such as may escape notice, may materially affect the result. It is, however, noteworthy that Palmaer (*Ber.*, 1888, 3260) has obtained only the two heteronucleal β-sulphonic acids on sulphonating α-nitronaphthalene. In view of the importance of the question raised, it is hoped that Cleve will ere long communicate a detailed account of his method which will make it easy to verify his conclusions.

17. "*The Action of Bromine and Chlorine on the Salts of Tetrethylphosphonium.*" By Orme Masson, M.A., D.Sc. (Edin.), and J. B. Kirkland, the University of Melbourne.

An account is given of experiments in continuation of those on the action of halogens on the salts of organic bases by Dobbin and Masson (*Chem. Soc. Trans.*, 1885 and 1886). The results show a very close general similarity between the polyhaloid-derivatives of tetrethylphosphonium and those of trimethylsulphine and of tetramethylammonium, previously described. The tendency to form solid polyhaloid compounds is, however, more marked. Thus, for instance, a crystalline tetrethylphosphonium tribromide, PEt_4Br_3, was obtained, whereas the previously described tribromides were unstable liquids; also a solid, but unstable, more highly brominated bromide, which was shown by synthetic experiments to have the composition PEt_4Br_7. Chlorine acting on the chloride gives only one compound, the trichloride, PEt_4Cl_3; but with the iodide it forms the tetrachloride, PEt_4ICl_4, which is converted by alcohol into the dichloriodide, PEt_4ICl_2. Quantitative synthetic experiments were made to ascertain whether the sulphate really resembles the haloid compounds; from these it appears that it closely resembles the bromide in its behaviour towards bromine and the chloride in its behaviour towards chlorine, both in the nature and appearance of the products and in their composition. The solid brominated sulphate, $(PEt_4)_2SO_4 \cdot Br_{12}$, yields the tribromide, PEt_4Br_3, when treated with alcohol. The most highly brominated derivative of the sulphate that could be obtained had the composition $(PEt_4)_2SO_4 \cdot Br_{22}$; but it is doubtful whether this really represents a definite compound. The following table contains a list of the new substances, the methods of forming them, and their most marked properties. The first formula is queried because the experimental evidence does not suffice to establish it, though analogy renders it probable. The eighth formula is queried because of the doubt already expressed as to the definite nature of the substance to which it is assigned.

18. "*The Preparation of the Salts of Triethylsulphine, Tetrethylphosphonium, and Analogous Bases.*" By Orme Masson, M.A., D.Sc. (Edin.), and J. B. Kirkland, University of Melbourne.

When sulphur is heated with ethyl iodide in sealed tubes at 180°, it entirely disappears and is converted into triethylsulphinetriiodide, $S + 3EtI = SEt_3I_3$; on treating this triiodide under water with hydrogen sulphide it is converted into the iodide, from which the hydroxide, &c., may be prepared. The yield is nearly a theoretical one.

The same process is applicable to the preparation of selenine salts from selenium, and of tetraethylphosphonium salts from phosphorus—either the ordinary or the red modification. In the case of phosphorus, however, a mixture of two different polyiodides is obtained: $2P + 7EtI = PEt_4I_3 + PEt_3I_4$. The second of these is converted by the treatment with hydrogen sulphide and water into triethylphosphine oxide, so that only half of the phosphorus goes to form the phosphonium salt,—

$$PEt_4I_3 + H_2S = PEt_4I + 2HI + S;$$
$$PEt_3I_4 + H_2S + H_2O = PEt_3O + 4HI + S.$$

The yield obtained is very nearly theoretical.

The use of silver hydroxide may be obviated by adopting Hofmann's potash process in recovering tetrethylphosphonium iodide from the solution obtained after the hydrogen sulphide treatment. The solution is saturated with potash and warmed, when the iodide forms an oily layer on the surface, which is readily separated and purified. This method works well, and it also answers in the case of the sulphine preparation.

The researches of Carius and of Crafts and Silva on the preparation of triethylphosphine oxide from phosphorus and ethyl iodide are criticised in the light of the results of the present investigation.

No.	Substance.	Method of formation.	Temperature of formation.	Chief properties.
1.	PEt_4IBr_4 (?).	Br_2 on iodide.	Cold	Bright red crystal, solid, unstable.
2.	PEt_4IBr_2.	Alcohol on 1.	—	Orange crystals, stable.
3.	PEt_4ICl_4.	Cl_2 on iodide.	70°	Yellow crystal mass, unstable.
4.	PEt_4ICl_2.	Alcohol on 3.	—	Yellow crystals, stable.
5.	PEt_4Br_7.	Br_2 on bromide.	110°	Scarlet crystal mass, unstable.
6.	PEt_4Br_3.	Alcohol on 5 or 9.	—	Red crystals, stable.
7.	PEt_4Cl_3.	Cl_2 on chloride.	110°	Yellow crystal mass, unstable.
8.	$(PEt_4)_2SO_4Br_{22}$ (?).	Br_2 on sulphate.	Cold	Red liquid, unstable.
9.	$(PEt_4)_2SO_4Br_{12}$.	,, ,,	110°	Red solid, unstable.
10.	$(PEt_4)_2SO_4Cl_4$.	Cl_2 ,, ,,	130°	Yellow solid, unstable.

PHYSICAL SOCIETY.

Annual General Meeting, February 9, 1889.

Prof. Reinold, F.R.S., President, in the chair.

The Reports of the Council and Treasurer were read and adopted. From the former it appears that the number of members has only slightly increased during the year, due, it is supposed, to the advantages offered by the Society not being generally known, and a fly-leaf has been prepared, giving a short account of the Society's objects and procedure, copies of which may be obtained from the Secretaries.

During the past year Vol. I., Part I,, of "Physical Memoirs selected and translated from Foreign Sources" has been printed and issued to members, and translations of important memoirs by Fourier, Hittorf, and Volta are well advanced, and will be published shortly.

The Treasurer's report showed the financial position of the Society to be very satisfactory.

Owing to the lamented death of Prof. Clausius, a vacancy has occurred in the list of Honorary Members, to fill which Prof. R. W. Bunsen was nominated by the Council and duly elected.

The following gentlemen were elected to form the new Council :—

President—Prof. A. W. Reinold, M.A., F.R.S.

Vice-Presidents—Dr. E. Atkinson; Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; The Right Hon Lord Rayleigh, M.A., D.C.L., Sec.R.S.

Secretaries—Walter Baily, M.A.; Prof. J. Perry, F.R.S.

Treasurer—Prof. A. W. Rücker, M.A., F.R.S.

Demonstrator—C. Vernon Boys, F.R.S.

Other Members of Council—Hon. R. Abercromby; T. H. Blakesley, M.A., M.Inst.C.E.; W. H. Coffin; Conrad W. Cooke; Prof. O. Lodge, D.Sc., F.R.S.; Prof. W. Ramsay, Ph.D., F.R.S.; W. N. Shaw, M.A.; Prof. S. P. Thompson, D.Sc.; H. Tomlinson, B.A.; G. M. Whipple, D.Sc.

Cordial votes of thanks were passed:—1st, To the Lords of the Committee of Council on Education for the Use of the rooms and apparatus of the Normal School of Science; 2nd, To the Council and Officers of the Society for their services during the past year; and 3rd, To the Auditors, Mr. Inwards and Prof. Minchin, for examining the accounts.

In returning thanks for the Council and Officers, the President attributed the great success of their meetings to the indefatigable zeal displayed by the Hon. Secretaries.

The meeting was then resolved into an Ordinary Science Meeting, at which Mr. James Wimshurst and Mr. Percy W. Sellon were elected Members.

Prof. A. S. Herschel, D.C.L., F.R.S., read a paper on "*Physico-Geometrical Models*," and exhibited a collection of geometrical figure models illustrating elementary forms of crystallographical and chemical form constructions.

The subject, he said, had suggested itself to him as an important one for study some five years ago, from the possibility which he then discovered of effecting a four-limbed mechanical cycle, similar to a thermo-dynamic cycle, with a conically revolving pendulum, the mathematical conditions of whose motion involved the logarithm of the circle radius of the knobs' revolution as a quantity equivalent to entropy in the thermal cycle. The mechanical cycle may be effected as follows:—Suppose the pendulum knob to be revolving at velocity V_1 and radius r_1; imagine the controlling force to decrease, so that the radius varies from r_1 to r_2, the velocity remaining constant at V_1; then increase the controlling force to its original value and simultaneously impart velocity to the knob to keep the radius constant at r_2, the final velocity being V_2. Next, further increase the controlling force so as to cause the radius to decrease to r_1 at velocity V_2, and finally, decrease the controlling force to its initial value, simultaneously retarding the knob till the velocity is V_1 at radius r_1. The nett energy concerned in the operations was given as $W=(V_1^2-V_2^2)\phi$, where $\phi=\log.\frac{r_1}{r_2}$, and the cycle affords an illustration of transformation of gyratory motion into energy of reverberatory push along the axis. The logarithm, ϕ, is also measured by the area of a hyperbolic sector, and is connected (as was shown) with a sector of the circle which a lamp's conical beam would inscribe upon a square glass screen or plate dividing a long room of square cross-section into two parts. The conical beam, prolonged through the glass, then traces, on the walls beyond, hyperbolas, whose sectors from their summits are related to the circles' corresponding sectors by a well-known hyperbolocyclic trigonometrical connection. From this mode of constructing the connection, and from a discordance which it shows at the asymptote extremities with Euclid's definition of parallel straight lines, the author concludes that cubic space cannot be continuous in its structure, but must be in a physically constructive sense, like material particles indestructively atomic or molecular. The models showed modes of constructing cubic space in various ways, chiefly by means of tetrahedra, octahedra, and dodecahedra, the common element of form in these being also shown to be the right-angled tetrahedron or "biquoin" obtained by dividing a cube into six equal parts by three planes through its diagonals.

A model of Sir W. Thomson's soap foam figure and some wooden models representing Haüy's polyhedral atoms and their combinations were exhibited to illustrate the structural view thus taken of geometry, and chemical figure models of the ring of tetrahedral carbon molecules in benzene, and of the asymmetric groups of similar atoms in active and inactive tartaric acid were shown.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Formerly, the action of nitrate of soda on the soil was imperfectly understood—whether due to the nitric acid present in the nitrate or to the soda. No tyro in agricultural chemistry would now dream of attributing it to the action of the soda. No more would, I feel convinced, the recent experimenters on ferrous sulphate attribute, as they all seem to me to have done, the action of this substance to its base alone, if they instituted comparative experiments with (1) sulphuric acid (highly dilute), (2) gypsum, (3) salt-cake, (4) sulphate of alumina, (5) sulphate of iron, using equivalents of sulphuric acid in each.

Has green vitriol any tendency to absorb ammonia from the atmosphere, or has the compound to which it is resolved in the soil any such tendency?

The result of the action of sulphuric acid in the form of sulphate of alumina upon the soil should be interesting, as alumina seems only to be present in the ash of the Lycopods. So far as I have followed these experiments the great bulk of them seem to have been upon sulphur-loving plants.

I should be glad if some one who has more time and opportunity than I have would undertake the experiments which I have indicated.—I am, &c.,

J. G. McIntosh.

THE FATAL EXPLOSION OF A GAS CYLINDER AT DUBLIN.

To the Editor of the Chemical News.

Sir,— The recommendation to make the couplings of different sizes would not prevent the man in charge of

the compressing pumps from accidentally putting coal-gas into the oxygen compressor, or *vice versa*, and then re-filling a returned half-empty bottle with the wrong gas. What the public require is perfect security, even if the gases have been accidentally supplied mixed. Bearing in mind that the most energetic combustion is at once arrested by contact with a sufficient quantity of cold metal, I believe that all risk of explosion would be avoided by attaching a spiral worm of fine copper tubing to the lower portion of the valve, so as to project into the bottle, through which worm the gases would have to pass before reaching the jet. If one coil was found insufficient, two, or even three coils could be used, one inside the other, without materially reducing the capacity of even the smallest sized bottle.

A Hemmings' safety jet, permanently fixed behind the valve and in the bottle, would, of course, have the same effect, but would, I fear, reduce the pressure at the burner too considerably to admit of its use.—I am, &c.,

CLEMENT J. LEAPER.

Technical Schools, Kevin Street, Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 4, January 28, 1889.

Reactions of Hydrogen Peroxide with Chromic Acid.—M. Berthelot.—If hydrogen peroxide is brought in contact with chromic acid in presence of a powerful mineral acid, such as sulphuric or hydrochloric acid used in excess, there is first produced the blue colouration of perchromic acid, followed by a slow escape of oxygen. The chromic acid is converted into chromic sulphate. Feebler acids, such as acetic and phosphoric, produce, with chromic acid and oxygenated water, a purple or violet colouration, due to a mixture of perchromic acid and of a brown compound. With more feeble acids, such as boric and hydrocyanic acids, the liquid merely turns brown. With pure potassium dichromate oxygenated water is decomposed to an indefinite extent. After the liquid, which at first turns brown, has resumed its original colour, on the addition of a fresh dose of oxygenated water the brown colour reappears. In twenty-four hours one equivalent of potassium dichromate has thus been found to decompose 40 equivalents of oxygenated water. At the end of the experiment the solution of dichromate retains its original composition, and contains no trace either of perchromic acid or of chromium oxide.

Butylic Ethers, Mixed and Properly So-called.—E. Reboul.—The author describes di-isobutylic ether, a secondary isobutylic ether, a tertiary isobutylic ether and di-secondary butylic ether, and the secondary-tertiary and ditertiary butylic ethers.

On the Gadolinium of M. de Marignac.—Lecoq de Boisbaudran.—This paper is a critique on certain researches of Mr. Crookes.—The author quotes certain passages quite correctly in English in a footnote, but modifies them very seriously in the body of his paper, imputing to Mr. Crookes assertions which he has never made, as anyone may see who takes the trouble to compare the footnote with M. de Boisbaudran's paraphrase and comments.

New Solvents for Prussian Blue; Easy Preparation of Ordinary Soluble Prussian Blue and of Pure Prussian Blue Soluble in Water.—Common Prussian blue and Turnbull's blue, when duly purified, appear identical. Ordinary Prussian blue may be rendered soluble by digestion for some days, or by boiling with a solution of potassium ferrocyanide or, preferably, ferricyanide. It may be at once prepared by adding gradually a hot solution of 70 parts crystalline ferrous sulphate to the boiling solution of 110 parts potassium ferricyanide, boiling for two hours and filtering, washing with pure water, and stopping when the washings run through deeply blue. Soluble blue gives, with metallic salts, a series of definite blue compounds. Molybdic acid and ammonium molybdate and tungstate dissolve Prussian blue readily.

Relations between Solubilities and Melting-Points.—A. Etard.—This paper requires the accompanying diagram.

Determination of Organic Nitrogen by Kjeldahl's Method.—C. Viollette.—On determining the nitrogen in maize-cake by this method and by those of Will-Varrentrapp and Dumas, the author obtains results closely agreeing, that by the soda-lime process being the lowest by 0·12 per cent. The Kjeldahl process does not economise time.

Compounds of Aniline with Chloric and Perchloric Acids.—Ch. Girard and L. L'Hote.—Aniline chlorate and perchlorate may be prepared by the direct action of the acids upon aniline, or the chlorate may be obtained by double decomposition. "Ordinary" nitric acid and hydrochloric acid react upon aniline chlorate without ignition, giving coloured products which the authors are studying.

Lime Combined in Soils.—Paul de Mondesir.—Most soils contain a noteworthy proportion of lime not in the state of carbonate, but capable of being removed by cold dilute acids.

No. 5, February 4, 1889.

Certain Reactions of Mercury Ammonium Chlorides.—M. André.—The precipitation of the two bodies above mentioned, effected in the cold, yields a series of compounds which are sometimes very complicated, and which are frequently mixtures in various proportions of Kane's mercuriammonium chloride or chloramidide (NH_2H_8Cl), and of dimercuriammonium chloride. This complexity depends on the action of an excess of water upon the chloramidide.

Separation of Zinc and Nickel.—H. Baubigny.—(See p. 88).

The Formation-heat of Aniline Bichromate.—Ch. Girard and L. L'Hote.

Alcoholic Combinations of Sodium Glycol-alcoholate.—M. De Forcrand.—These two thermochemical papers do not admit of useful abstraction.

The Acetonic Function of Nitro-camphor; its Hydrochloration and its Polymerisation.—P. Cazeneuve.—The author describes reactions showing the acetonic function of nitro-camphor. He then explains the formation of nitro-camphor hydrochlorate, its decomposition by alcoholised water yielding a hydrate and subsequently a polymer with a phenolic function.

Determination of Organic Nitrogen by Kjeldahl's Process.—E. Aubin and M. Alla.—The authors, in reply to a paper by M. L'Hote (*Comptes Rendus*, Jan. 7, 1889), describe the manner in which they have carried out the process. They took 0·5 grm. of nitrogenous organic matter, 20 c.c. of pure sulphuric acid at 66°, and 0·5 grm. of mercury. The operation did not exceed ninety minutes, and the liquids obtained were clear and colourless. The authors conclude that Kjeldahl's method is trustworthy and accurate, the results being equal, if not superior, to those obtained with soda-lime. The organic matter is completely transformed during the operation, and all the nitrogen is recovered as ammonia. There is no loss of ammonia during the operation.

Journal fur Praktische Chemie.
Vol. xxxix., No. 1.

On Metallic Diamine Compounds.—S. M. Jorgensen.—The author has obtained and examined platinum and cobalt bases in which ethylene-diamine takes the place of ammonia, and finds then exceedingly stable. In this memoir he describes the salts of platino-ethylene-diamine, the ethylene-diamine-luteo-cobaltic and the dichloro-praseo-cobaltic salts.

Diazo- and Azo-compounds of the Fatty Series, No. IV.—Th. Curtius and R. Jay.—This paper, which treats of hydrazine, is too extensive for abstraction.

Researches from the Laboratory of the University of Freiburg.—These consist of a paper by Ad. Claus and J. Hirsch on Metakresol.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 3.

The Presence of the Vapour of Benzene in Coal-Gas, and on its Determination.—M. Berthelot.—Already noticed.

Chemical Constitution of Spongine.—M. P. N. Zalocostas.—Spongine approximates in its constitution to the collagenous substances.

MEETINGS FOR THE WEEK

Monday, 25th.—Medical, 8.30.
Tuesday, 26th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Society of Arts, 8. "English Bookbinding in the Reign of Henry VIII.," by W. H. J. Weale.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 27th.—Society of Arts, 8. "The Irish Lace Industry," by Alan S. Cole.
Thursday, 28th.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Institute of Electrical Engineers, 8.
Friday, March 1st.—Royal Institution, 9. "Leigh Hunt," by Edmund Gosse, M.A.
Saturday, 2nd.—Royal Institution, 3 "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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THE TRUE POSITION OF PATENTEES. By Henry Moy Thomas. Explaining the regulations now in force in all the principal countries and the combined effects of Home, Foreign, and Colonial Patent Laws.

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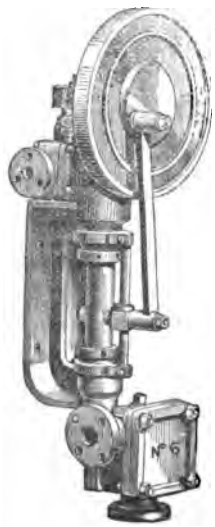

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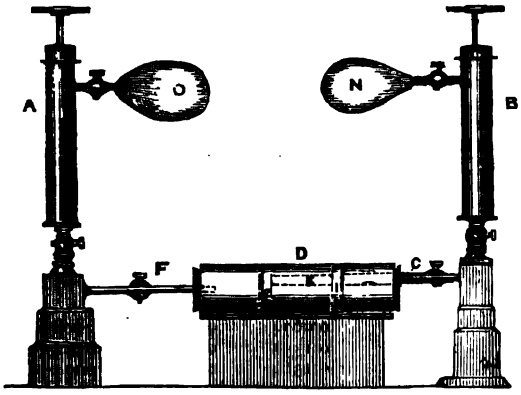
THE CHEMICAL NEWS.

Vol. LIX. No. 1527.

THE PARTIAL SEPARATION OF OXYGEN FROM THE ATMOSPHERE BY MEANS OF EXOSMOSE.

By H. N. WARREN, Research Analyst.

The diffusion or osmotic properties of a gas, when compared with another of opposed density, has been pointed out from an early date, perhaps one of the simplest means of observing the same being the swift passage of hydrogen gas when in admixture with one of greater density, through the pores of a moist membrane. So perfect, however, is this peculiar separation in the case of hydrogen when in admixture with an equal bulk of oxygen, the operation being performed in a caoutchouc bag kept weighted, that on examining the same after an hour's duration a sufficiency of hydrogen will be observed to have escaped, so as to totally destroy the explosive nature of the mixture. By taking advantage of the peculiarity of caoutchouc to condense gases upon its surface, an apparatus has been lately constructed, and intended for the parting or partial separation of oxygen gas from the atmosphere as explained by the accompanying figure. It is composed of two somewhat powerful exhausting syringes, A and B, the top extremity of each being provided with a cock, and connected to the same two small gas bags, the bottom, or further ex-



tremity of each syringe being connected with a porous pot, D, provided internally with two discs of compressed charcoal, and charged with a preparation of finely-divided caoutchouc, obtained by immersing the same, before using, in a solution of caoutchouc in naphtha. The outer wall of the porous cylinder is also provided with a tightly fitting jacket of very thin rubber, the pipe, E, in connection with the cork, C, being pierced with two small orifices, and terminating at the commencement of the second disc, and intended to remove the nitrogenous atmosphere remaining in the cylinder after the separation of the oxygen by means of the A syringe. The piston rod of the syringe, A, being now raised upwards, a vacuum is naturally produced within the porous cylinder, D, and being surrounded by the atmosphere, an inward pressure is at once experienced, the result being that the cylinder is partially filled with an atmosphere extremely rich in oxygen, and also with one in which nitrogen predominated largely, which, by working the piston on either side of the cylinder with due care, may be collected in their respective bags, namely, O and N, intended for the reception of the same. On submitting both portions of these separated gases to examination, that portion obtained from the syringe, A, was found to be sufficiently rich in oxygen to readily re-kindle a glowing splint, and even support the combustion of iron wire, results of several analyses proving an existence of 50 per cent of oxygen, while the nitrogenous atmosphere collected by the opposite cylinder readily extinguished a lighted match when introduced into the same. By a slight alteration in the arrangement of the apparatus a mixture of hydrogen and oxygen were separated so effectively as to produce only the minutest quantity of water when separately made to ignite. Carbonic anhydride and various other gases in admixture with one another were experimented upon with a like result.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

COTTON-SEED OIL AND BEEF FAT IN LARD.

By J. A. WILSON.

Up to some time ago the positive detection, not to say the approximate determination, of cotton-seed oil and beef fat in lards was of a difficult character, but the discovery of certain optical and general tests has rendered this problem tolerably easy. Some time ago the author had reason to examine two samples of old cotton-seed oil, which had been in the laboratory thirteen and seventeen months respectively, and although the samples responded clearly to the general tests, on applying the silver test in the different forms prescribed, no reduction occurred alone or when mixed with genuine lard. Here then we have a serious objection to these silver tests, for the matter causing reduction of silver nitrate seems to be destroyed by keeping; hence a reaction with silver nitrate proves the presence of cotton oil, but no reaction does not prove the absence in lard.

Chemists having old samples of oil in their possession will render service by trying the silver nitrate reaction on the oils. It is to be remarked here that I tried the reaction on the fatty acids produced by saponification, with a negative result. By acting on the oil by sulphur chloride, small percentages of cotton oil can be detected.

Researches on this subject have been published by Mr. Warren. Some time ago the author made some experiments on the surface tension tests for oils. Pure dry melted lard, dropped on water of 100° F., does not extend or increase in size. Beef fat or mutton fat extends over the surface of the basin, breaking up into innumerable droplets, and is agitated by a rapid gyratory motion.

The author mixed pure lard with 10, 15, 20, and 25 per cent of beef fat, and allowed one drop to fall on water of 100° F. By noticing the degree of expansion and the time required, approximate determinations of the beef fat can be obtained. Mutton fat behaves similarly, and therefore cannot be distinguished. On repeating this with exactly the same lard eight months after, the drop behaved exactly like beef or mutton fat, this being most unfortunate. The only other test is the delicate test with iodo-mercuric chloride of Hubl. This method is one of the most delicate and best in the chemistry of oils and fats. The author's experience is most extensive, its results are exact and reliable. Somewhat discrepant statements exist, however, as to the iodinic absorption of cotton-seed oil and lard. Thus Pattinson (*Journal Society Chem. Industry*, No. 1, vol. viii.) gives from 57 to 63 per cent iodine absorbed by lard, and 105 to 116 per cent for cotton oil. The author has never found more than 60 per cent for lard and 110 per cent for cotton-seed oil. Again, Pattinson gives 41 per cent for beef fat, whilst my figures approach the average, 44 per cent. It is needless to say these different statements would cause grave errors in calculating the foreign fat in a sample of lard

It would be of great service if chemists would state their experience of this most excellent test. In my opinion no satisfactory statement of the amount of beef fat or stearin can be given in lard containing cotton-seed oil. The following table gives the maximum and minimum absorptions of iodine in the common oils I have found:—

Name of Oil or Fat.	Maximum Absorption. Per cent.	Minimum Absorption. Per cent.
Cotton-seed Oil	110·11	106·0
Linseed ,, ...	149·10	148·07
Rape Oil (Stettin) ..	102·76	100·43
Castor ,, ..	83·40	—
Palm ,, ..	52·40	51·01
Olive ,, ..	84·00	78·50
Neatsfoot,, ..	70·70	70·00
Cocoanut,, ..	9·35	8·97
Lard	60·00	57·10
Beef Fat	44·00	43·26
Mutton,, ...	46·19	45·18
Bone ,, ...	49·58	46·27
Tallow	41·98	40·01

The Laboratory,
Tottington Mill, near Bury.

SEPARATION OF ALUMINIUM AND ZIRCONIUM.*

By I. THOMAS DAVIS, Jr.

While studying some of the iodine compounds of zirconium it was found that the iodate, when precipitated from neutral or very feebly acid solutions, gave filtrates in which no zirconium could be detected with ammonia. This apparent insolubility and the fact that aluminium iodate, according to Berzelius,† was deliquescent, suggested the possibility of separating these metals by means of an alkaline iodate. Solutions of aluminium refused to show the least signs of precipitation when treated in a manner similar to that by which complete precipitation had been obtained from zirconium salts. In order to examine the method quantitatively, a solution of zirconium chloride in hydrochloric acid was employed. This solution was prepared as follows:—

Zircon was decomposed with sodium carbonate and hydrate, the fusion boiled out repeatedly with water, and the residual sodium zirconate decomposed with sulphuric acid. This solution was evaporated carefully to dryness, and kept at a heat just below redness for half an hour. It was then dissolved in water, to which a little sulphuric acid had been added, and precipitated with ammonia. The resulting hydrate was dissolved in hydrochloric acid, and the zirconium precipitated several times with sodium thiosulphate to separate the last trace of iron. The zirconium was finally precipitated with ammonia, washed until the filtrate no longer reacted for chlorine, dissolved in hydrochloric acid, which was added in sufficient quantity to prevent the deposition of an oxychloride, and diluted to the proper strength. It contained in round numbers 5 per cent of hydrochloric acid by weight.

In order to standardise this solution the zirconium was precipitated with ammonia, using to a certain extent the same precautions which are to be observed when aluminium is precipitated in a similar manner, and Nos. (1) and (2) represent duplicate determinations.

Weight of solution.	ZrO_2 found.	ZrO_2 in 25 grms.
(1) 25·344 grms.	0·1696 grm.	0·1673 grm.
(2) 25·322 ,,	0·1686 ,,	0·1669 ,,

The average, 0·1671 grm., has been taken as representing the correct amount of the tetrachloride, $ZrCl_4$, in terms of the dioxide, ZrO_2, in 25 grms. of the solution.

Qualitative experiments seemed to point to the possibility of complete precipitation, as an oxyiodate, when the solution contained a moderate amount of free acid.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(3) 25·325	0·1693	0·1604	0·0089−
(4) 25·297	0·1691	0·1576	0·0115−

In (3) and (4) the acid was neutralised with sodium carbonate, and hydrochloric acid added in such quantity that the solutions contained 1 per cent by weight. Sodium iodate was then added in excess, and the solutions brought to a boil, and fifteen minutes afterwards filtered, washed with hot water until the filtrate and washings in each case amounted to about 400 c.c. They were dried and ignited together with the filters. During the ignition slight explosions took place, and once the lid of the crucible, which contained (4), was thrown off. At the same time it took prolonged ignition at the highest heat of the blast-lamp to arrive at constant weight, small quantities of iodine vapours being evolved. These vapours were due to sodium iodate retained by the precipitate, as the zirconium salt seems to part with its iodine at a heat below redness. Hence the idea of igniting this iodate or of precipitating zirconium from solutions containing much acid was abandoned.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(5) 20·300	0·1357	0·1380	0·0023+
(6) 20·159	0·1347	0·1349	0·0002+

In (5) and (6) the acid of the zirconium solution was neutralised with sodium carbonate, which was added until a permanent precipitate was formed. This was dissolved in the smallest possible quantity of dilute hydrochloric acid, sodium iodate added in excess, and the solutions boiled for fifteen minutes. Instead of filtering immediately, as in (3) and (4), it was thought safest to allow them to stand some time. They were therefore allowed to stand over night, then filtered, washed with hot water, dissolved in hydrochloric acid, of which it took a considerable amount, even while hot, precipitated with ammonia, ignited, and weighed. Unfortunately in (5) the washing was very imperfect, but in (6) and all subsequent experiments the washing was continued until the filtrates no longer gave a reaction for chlorine.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(7) 10·086	0·0674	0·0674	0
(8) 10·088	0·0674	0·0682	0·0008+
(9) 20·263	0·1354	0·1352	0·0002−
(10) 20·408	0·1364	0·1365	0·0001+

(7), (8), (9), and (10) were carried on exactly like (5) and (6), with the exception that to (9) 5 grms. of sodium chloride were added, and to (10) 10 grms. Precipitation seems to be complete, and sodium chloride is without action on the iodate. In filtering the iodate, which is flocculent, it is safest to use Swedish paper, as the precipitate can be more readily washed off without loss than from some of the other papers used.

These experiments having turned out so satisfactorily, it was thought possible that complete precipitation might take place in solutions containing some free acid, but not nearly in such quantity as had been employed in (3) and (4). To determine this point, (11) and (12) were made.

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(11) 30·337	0·2028	0·1996	0·0032−
(12) 30·410	0·2032	0·2010	0·0022−

The acid was neutralised as before and enough hydrochloric acid added to make the solution contain about 0·1 per cent of it. Aluminium chloride was also added in quantity about three times that of the zirconium chloride

* *American Chemical Journal*, Vol. xi., No. 1.
† *Lehrb.*, ed. 1843—48, iii., 479.

present. The solution of aluminium chloride was prepared by precipitating pure potassium alum several times to separate all sulphuric acid, and the hydrate dissolved in hydrochloric acid. Its strength was only approximately known. It is evident that precipitation, even in the presence of this small amount of acid, is incomplete. However, no aluminium seems to have been thrown down. The solutions, then, previous to precipitation, must be nearly neutral. Therefore in (13—14) and (15—16) the precipitation was carried on as in (5) and (6).

Weight of solution.	ZrO_2 used.	ZrO_2 found.	Error.
(13) 10·097	0·0675	0·0673	0·0002 –
(14) 10·070	0·0673	0·0671	0·0002 –
(15) 49·490	0·3308	0·3302	0·0006 –
(16) 49·398	0·3302	0·33·01	0·0001 –

In (13) and (14) the quantity of aluminium was about three times that of the zirconium, while in (15) and (16) equal quantities were used. These numbers seem to be within the error of analysis. Therefore to separate these two metals I proceed as follows:—Their solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is dissolved in the smallest possible quantity of dilute hydrochloric acid, and sodium iodate added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand twelve hours, filtered, washed down with boiling water, dissolved in hydrochloric acid, and finally precipitated with ammonia, ignited, and weighed. A convenient strength of solution is 100 m.grms. ZrO_2 in 100 c.c.

Three analyses of the zirconium salt proved it to be an oxyiodate of variable composition. Several attempts were made to separate iron, both in the ferrous and ferric state, but without success. This metal must be removed from the mixture of aluminium and zirconium previous to their treatment with sodium iodate.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 89).

METHODS OF ANALYSES OF DAIRY PRODUCTS.

BUTTER.

Microscopic Examination.

PLACE a small portion of the fresh sample, taken from the inside of the mass, on a slide, add a drop of pure sweet-oil, cover with gentle pressure, and examine with a one-half to one-eighth inch objective for crystals of lard, &c.

Examine same specimen with polarised light and selenite plate without the use of oil.

Pure fresh butter will neither show crystals nor a particoloured field with selenite. Other fats, melted and cooled and mixed with butter, will usually present crystals and variegated colours with the selenite plate.

Specific Gravity.

Take a specific gravity flask, not graduated, the stopper of which carries a delicate thermometer, whose bulb occupies sensibly the centre of the flask. The thermometer should be first compared with a standard instrument.

Clean the picnometer with water, alcohol, and ether; dry, be careful to remove all the ether vapour, and weigh.

Fill with distilled water, insert stopper, and place in vessel containing water which comes nearly to top of picnometer (without stopper); gradually raise the temperature of water in vessel containing flask until it is 40·5° to 41° C.

The moment the thermometer of the picnometer marks 40° remove the flask, dry carefully, cover capillary safety-tube, and set in balance or desiccator to cool. Weigh when temperature falls nearly to that of balance-room. Having determined the titre of the flask, it is to be carefully dried, filled with the melted and filtered fat at a temperature below 40°, and the weight of the fat determined at 40°, as directed above.

Melting-point.

Apparatus.—The apparatus consists of (1) an accurate thermometer, for reading easily tenths of a degree; (2) a less accurate thermometer for measuring the temperature of water in the large beaker glass; (3) a tall beaker glass, 35 c.m. high and 10 c.m. in diameter; (4) a test-tube 30 c.m. high and 3·5 c.m. in diameter; (5) a stand for supporting the apparatus; (6) some method of stirring the water in the beaker—for example, a blowing-bulb of rubber and a bent glass tube extending to near the bottom of the beaker; (7) a mixture of alcohol and water of the same specific gravity as the fat to be examined.

Manipulation.—The discs of the fat are prepared as follows:—The melted and filtered fat is allowed to fall from a dropping tube from a height of 15 to 20 c.m. on to a smooth piece of ice floating in water. The discs thus formed are from 1 to 1½ c.m. in diameter, and weigh about 200 m.grms. By pressing the ice under the water the discs are made to float on the surface, whence they are easily removed with a steel spatula.

The mixture of alcohol and water is prepared by boiling distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot the water is poured into the test-tube already described until it is nearly half full. The test-tube is then filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled the mixture will contain so many air-bubbles as to be unfit for use. These bubbles will gather on the disc of fat as the temperature rises and finally force it to the top of the mixture.

The test-tube containing the alcohol and water is placed in a vessel containing cold water, and the whole cooled to below 10° C. The disc of fat is dropped into the tube from the spatula, and at once sinks until it reaches a part of the tube where the density of the alcohol-water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disc. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disc the thermometer is moved from time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days; in fact, until the air-bubbles begin to attach themselves to the disc of fat. In no case did the two liquids become so thoroughly mixed as to lose the property of holding the disc at a fixed point, even when they were kept for several weeks.

In practice, owing to the absorption of air, it has been found necessary to prepare new solutions every third or fourth day.

The disc having been placed in position, the water in the beaker-glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol-water mixture rises to about 6° below the melting-point, the disc of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

is even with the centre of the bulb. The bulb of the thermometer should be small so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, which might be done with a kind of clockwork. The rise of temperature should be so regulated that the last 2° of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. It is not necessary to cool the water in the bath. The test-tube (ice-water being used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1·5° above the melting-point of the fat under examination.

Working thus with two tubes about three determinations can he made in an bour.

After the test-tube has been cooled the globule of fat is removed with a small spoon attached to a wire before another disc of fat is put in.

Volatile Acids.

Take about 2·5 grms. filtered fat in 200 c.c. flask, to be used in subsequent distillation; add 2 c.c. aqueous solution potassium hydrate containing 0·5 grm. KOH per c.c. Add 2 c.c. 95 per cent alcohol and heat on water-bath, with occasional agitation. Saponification is complete in a few minutes. Evaporate until alcohol is all driven off, using a current of air to remove alcoholic vapour. The flask is fitted with a delivery tube and condenser. The delivery tube is carried up about 8 inches before it is bent to enter the condenser, and a bulb is blown in it just below the elbow, and this is filled with broken glass or glass-wool.

The fatty acids are then set free with 20 c.c. of a solution of phosphoric acid, made by dissolving 200 grms. glacial phosphoric acid in water and making up to 1 litre. Enough water is added to make the volume of liquid in the flask 70 c.c. Distillation is continued until the distillate measures 50 c.c., which is titrated with N/10NaOH, using phenol-phthalein as indicator.

(Care should be taken to have the potash used free from carbonate. A potash containing carbonate saponifies a fat with great difficulty. In an instance where the saponification was taking place very slowly, the potash was found to contain 6·80 per cent CO_2, equal to 21·17 per cent K_2CO_3).

Soluble Acids.

The washings obtained in the process of estimating the insoluble acids, the description of which follows, are made up to one litre, and an aliquot part taken for titration with one-tenth N alkali, using phenol-phthalein as indicator.

METHOD FOR THE DETERMINATION OF SOLUBLE AND INSOLUBLE ACIDS.

Reagents.

1. A standard semi-normal hydrochloric acid solution, accurately prepared.

2. A standard decinormal soda solution, accurately prepared; each 1 c.c. contains 0·0040 grm. of NaOH, and neutralises 0·0088 grm. of butyric acid, $C_4H_8O_2$.

3. An approximately semi-normal alcoholic potash. Dissolve 40 grms. good stick potash in one litre of 95 per cent alcohol, redistilled. The solution must be clear and the KOH free from carbonates.

4. A 1 per cent solution of phenol-phthalein in 95 per cent alcohol.

Saponification is carried out in rubber-stoppered beer-bottles holding about 250 c.c.

About 5 grms. of the melted butter fat, filtered and freed from water and salt, are weighed out by means of a small pipette and beaker, which are re-weighed after the sample has been taken out and run into a saponification bottle; 50 c.c. of the semi-normal potash is added, the bottle closed and placed on the steam-bath until the contents are entirely saponified, facilitating the operation by occasional agitation. The alcoholic potash is measured always in the same pipette and uniformity further insured by always allowing it to drain the same length of time, viz., thirty seconds. Two or three blanks are also measured out at the same time and treated in the same way.

In from five to thirty minutes, according to the nature of the fat, the liquid will appear perfectly homogeneous, and when this is the case the saponification is complete, and the bottle may be removed and cooled. When sufficiently cool the stopper is removed and the contents of the flask rinsed with a little 95 per cent alcohol into an Erlenmeyer flask of about 250 c.c. capacity, which is placed on the steam-bath, together with the blanks, until the alcohol has evaporated.

Titrate the blanks with semi-normal HCl, using phenol-phthalein as an indicator. Then run into each of the flasks containing the fat acids 1 c.c. more semi-normal HCl than is required to neutralise the potash in the blanks. The flask is then connected with a condensing tube three feet long, made of small glass tubing, and placed on the steam-bath until the separated fatty acids form a clear stratum on the surface of the liquid. The flask and contents are then allowed to become thoroughly cold, ice water being used for cooling.

The fatty acids having quite solidified, the contents of the flask are filtered through a dry filter-paper into a litre flask, care being taken not to break the cake. Two hundred to three hundred c.c. of hot water is next poured on the contents of the flask, the cork with its condenser tube re-inserted, and heated on the steam-bath until the cake of acids is thoroughly melted, the flask being occasionally agitated with a circular motion, so that none of its contents are brought on the cork. When the fatty acids have again separated as an oily layer the flask and its contents are cooled in ice water, and the liquid filtered through the same filter into the same litre flask. This treatment with hot water, followed by cooling and filtration of the wash water, is repeated three times, the washings being added to the first filtrate. The mixed washings and filtrate are next made up to 1 litre, and 100 c.c., in duplicate are taken and titrated with decinormal NaOH. The volume required is calculated to the whole liquid. The number so obtained represents the measure of decinormal NaOH neutralised by the soluble fatty acids of the butter fat taken, plus that corresponding to the excess of the standard acid used, viz., 1 c.c. The amount of soda employed for the neutralisation is to be diminished, for the 1 litre, by 5 c.c., corresponding to the excess of 1 c.c. ½ N acid.

This corrected volume, multiplied by the factor 0·0088, gives the butyric acid in the weight of butter fat employed. (See table).

The flask containing the cake of insoluble fat acids is inverted and allowed to drain and dry for twelve hours, together with the filter-paper through which its soluble fatty acids have been filtered. When dry the cake is broken up and transferred to a weighed glass evaporating dish. Remove from the dried filter-paper as much of the adhering fat acids as possible and add them to the contents of the dish. The funnel, with the filter-paper, is then placed in an Erlenmeyer flask, a hole is made in the bottom of the filter-paper, and it is thoroughly washed with absolute alcohol from a wash-bottle. The flask is rinsed with the washings from the filter-paper and pure alcohol, and these transferred to the evaporating dish. The dish is placed on the steam-bath and the alcohol driven off. It is then transferred to the air-bath and dried at 100° C. for two hours, taken out, cooled in a desiccator, and weighed. It is then again placed in the air-bath and

Table for the Calculation of Soluble Fatty Acids.

No. c.c. KOH sol.	Equiv. Grms.	N 10NaOH.	Equiv. Grms.	N/10NaOH.	Equiv. Grms.	N/10NaOH.	Equiv. Grms.
10	0·088	+0·25	0·0902	+0·50	0·0924	+0·75	0·0946
11	0·0968	0·25	0·0990	0·50	0·1012	0·75	0·1034
12	0·1056	0·25	0·1078	0·50	0·1100	0·75	0·1122
13	0·1144	0·25	0·1166	0·50	0·1188	0·75	0·1210
14	0·1232	0·25	0·1254	0·50	0·1276	0·75	0·1298
15	0·1320	0·25	0·1342	0·50	0·1364	0·75	0·1386
16	0·1408	0·25	0·1430	0·50	0·1452	0·75	0·1474
17	0·1496	0·25	0·1518	0·50	0·1540	0·75	0·1562
18	0·1584	0·25	0·1606	0·50	0·1628	0·75	0·1650
19	0·1672	0·25	0·1694	0·50	0·1716	0·75	0·1738
20	0·1760	0·25	0·1782	0·50	0·1804	0·75	0·1826
21	0·1848	0·25	0·1870	0·50	0·1892	0·75	0·1914
22	0·1936	0·25	0·1958	0·50	0·1980	0·75	0·2002
23	0·2024	0·25	0·2046	0·50	0·2068	0·75	0·2090
24	0·2112	0·25	0·2134	0·50	0·2156	9·75	0·2178
25	0·2200	0·25	0·2222	0·50	0·2244	0·75	0·2266
26	0·2288	0·25	0·2310	0·50	0·2332	0·75	0·2354
27	0·2376	0·25	0·2398	0·50	0·2420	0·75	0·2442
28	0·2464	0·25	0·2486	0·50	0·2508	0·75	0·2530
29	0·2552	0·25	0·2574	0·50	0·2596	0·75	0·2618
30	0·2640	0·25	0·2662	0·50	0·2684	0·75	0·2706

dried for another two hours, cooled as before, and weighed. If there is no considerable decrease in weight the first weight will do; otherwise, re-heat two hours and weigh. This gives the weight of insoluble fat acids in the quantity taken, from which the percentage is easily calculated.

The table gives the weight of the soluble fatty acids (butyric, &c.) for each quarter of a c.c. of decinormal alkali from 10 to 30.

Example :—

	Grms.
Weight fat taken	4·967
No. c.c. N/10 alkali used	25·50
Less 5 c.c. due to 1 c.c. N/2 acid	20·50
Weight soluble fat acids	0·1804
Per cent soluble fat acids	3·63

Saponification Equivalent.

About 2·5 grms. butter fat (filtered and free from water) are weighed into a patent rubber-stoppered bottle, and 25 c.c. approximately semi-normal alcoholic potash added. The exact amount taken is determined by weighing a small pipette with the beaker of fat, running the fat into the bottle from the pipette and weighing beaker and pipette again. The alcoholic potash is measured always in the same pipette, and uniformity further ensured by always allowing it to drain the same length of time (thirty seconds). The bottle is then placed in the steam-bath, together with a blank containing no fat. After saponification is complete and the bottles cooled, the contents are titrated with accurately semi-normal hydrochloric acid, using phenol-phthalein as an indicator. The number of c.c. of the acid used for the sample deducted from the number required for the blank gives the number of c.c. which combines with the fat, and the saponification equivalent is calculated by the following formula, in which W equals the weight of fat taken in m.grms. and N the number of c.c. which have combined with the fat.

$$\text{Sap. Equiv.} = \frac{2W}{N}.$$

If it is desirable to express the number of m.grms. of potash for each grm. of fat employed it can be done by dividing 5610 by the saponification equivalent and multiplying the quotient by ten.

Water.

Place about 2 grms. in flat-bottomed platinum dish two-thirds full of clean, dry sand and heat for two hours in air-bath at 105° C. (For alternate method of estimation of water, see later on).

Estimation of Salt.

Volumetric Method.—The amount of the butter, or butter substitute, to be taken is 5—10 grms.; weigh in a counterpoised beaker-glass. The butter (fresh from the refrigerator) is placed in portions of about 1 grm. at a time in the beaker, these portions being taken from different parts of the sample. By this means a reasonably fair sample of the whole is obtained.

The given quantity having been weighed out, it is removed from the pan.

Hot water is now added (about 20 c.c.) to the beaker containing the butter, and after it has melted the liquid is poured into the bulb of the separating apparatus. The stopper is now inserted and the contents shaken for a few moments.

After standing until the fat has all collected on top of the water, the stop-cock is opened, and the water, containing most of the salt, is allowed to run into an Erlenmeyer flask, being careful to let none of the fat globules pass.

Hot water is again added to the beaker and thence poured into the separatory apparatus, the bottle well shaken, and the foregoing process is repeated ten to fifteen times, using each time 10 to 20 c.c. of water.

The resulting washings contain all but a mere trace of the NaCl originally present in the butter.

Estimation of NaCl in Filtrate.—The chloride of sodium is now determined in the filtrate by a standard solution of $AgNO_3$, using a few drops of a saturated solution of potassium chromate as indicator.

Total Mineral Matter. (Ash) and Curd.

The methods of estimating curd depend on the principle of first drying a weighed portion of the butter, and afterwards extracting the fat with ether or petroleum. The residual mass is then weighed and the curd determined by loss on ignition. This process is carried on as follows :—

Five to ten grms. of butter fat are dried at 100° C. for a few hours in a porcelain dish. The dried fat, &c., is filtered through a Gooch crucible, the contents of the dish are all brought into the crucible and well washed with ether or light petroleum. The filter crucible is dried for two hours in air-bath and weighed. The curd is then determined by loss of weight on ignition.

The total mineral matter is represented by the residue left after ignition.

Curd and insoluble substances may be estimated somewhat more accurately as follows:—

Place the butter (5 to 10 grms.) in a Gooch crucible; set the crucible on a pad of blotting-paper in an air-bath (100° C.) for an hour, wash two or three times with ether or light petroleum. Dissolve the salt with hot water, dry at 100° C., and weigh. Any insoluble mineral matter and the ash of the curd is weighed with it in this method.

Casein.

Method of Babcock.—Ten grms. of the dried butter are treated with light petroleum until all fat is removed. The residue is then ignited with soda-lime or treated by the Kjeldahl method.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. A. E. Tutton was formally admitted a Fellow of the Society.

It was announced that the following changes in the Council List were proposed by the Council:—

As *President*, Dr. W. J. Russell, F.R.S., *vice* Mr. Crookes, F.R.S.

As *Vice-Presidents*, Professor J. Emerson Reynolds, F.R.S., and Mr. R. Warington, F.R.S., *vice* Mr. Howard and Prof. Schorlemmer, F.R.S.

As *Treasurer*, Prof. Thorpe, F.R.S., *vice* Dr. Russell, F.R.S.

As *Members of Council*, Mr. Norman Collie, PhD., Professor John Ferguson, M.A., Mr. S. U. Pickering, M.A., and Mr. J. F. M. Page, *vice* Profs. Carnelley, P. F. Frankland, and Ramsay, F.R.S., and Mr. Friswell.

Messrs. R. H. Davies, R. J. Friswell, and S. Rideal were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. John Leigh Hoskyns-Abrahall, Norman Villa, Rusholme, Manchester; James Annal, 3, Reid Street, Dundee; Richard Douglas Bailey, City Brewery, Gloucester; Henry Richardson Hoyles, c/o Messrs. Treacher and Co., Bombay; Clement Joseph Leaper, 4, Chester Road, Ranelagh, Dublin; George T. Wilkinson Newsholme, 74, Market Place, Sheffield; Richard W. Roberts, 22, Calle Arturo Prat, Valparaiso, Chili; Thomas Alexander Shegog, 39, St. Mary's Road, Dublin; Henry Simmons, 9, Christ Church Terrace, Cheltenham; Patrick Alexander Weir, M.B., Ghazipur, N.W.P., India; Charles Wood, 5, Woodview, Bradford, Yorks.

The following were elected Fellows of the Society:—Messrs. P. Carmody, Edward Mitchell Chaplin, John W. Clayton, John Curragh, Philip Norman Evans, Robert Ferguson, M.A., David Ferrier, Conrad Gerling, Alfred Miall Hanson, John Joseph Hickey, William H. Jowett, William E. Lauer, George McCalman, Harry East Miller, Arthur F. Morgan, Henry Joshua Phillips, George Arthur Pingstone, Harry Hollis Robins, Stanley Southam, James Speakman, Thomas B. Stillman, George Sherbrooke Turpin, M.A., B.Sc., Thomas John Underhill.

The following papers were read:—

19. "*Note on the Decomposition of Potassic Chlorate by Heat in the presence of Manganic Peroxide.*"

Having observed the alteration in appearance that peroxide of manganese undergoes when heated with potassic chlorate, the author has made a number of experiments, using different kinds of oxide of manganese, determining the loss of weight that the mixture suffers when heated, and also the quantity of chlorine simultaneously generated. The heating was generally effected by the vapour of boiling mercury, at which temperature the potassic chlorate is not changed. The more finely divided the peroxide, the more rapid is the action and the more chlorine is evolved. When the evolution of chlorine is prevented by the addition of a small quantity of sodic or potassic carbonate, the decomposition of the chlorate proceeds very slowly, unless the temperature be raised much above that of boiling mercury. When potassic chlorate is fused with a minute quantity of peroxide of manganese, the residue is found to be pink on cooling, indicating the presence of a permanganate: and inasmuch as potassic permanganate is decomposed at a temperature of 275°, it is not improbable that the permanganate is decomposed by the heat as rapidly as it is produced into potassic manganate, manganic peroxide, and oxygen; the resulting potassic manganate is acted on by chlorine generated by the action of the peroxide on some fresh chlorate, forming potassic chloride, manganic peroxide, and oxygen, so that the peroxide is being continually reproduced. The quantity of chlorine evolved corresponds to only a very small proportion of the manganic peroxide present, so if the first action really takes place the chlorine must be absorbed and employed in converting the potassium into chloride.

Discussion.

Professor Thorpe, referring to the well-known fact that no perchlorate is formed in presence of manganese dioxide, asked how this was to be explained.

Mr. Williams stated that he had been unable to obtain the theoretical amount of oxygen from potassium chlorate by heating it *in vacuo*: a gas was given off which attacked mercury—presumably chlorine, and therefore it was probable that the residue contained potassium peroxide. On heating silver iodate *in vacuo* the theoretical amount of oxygen was obtained without difficulty.

Professor McLeod said that he was unable to account for the non-production of perchlorate in presence of manganese dioxide; as potassium perchlorate was not decomposed by heating with manganese dioxide, it probably was not even an ephemeral product. He had without difficulty obtained almost the theoretical amount of oxygen from chlorate. He did not think that the pink colour was due to ferrate as had been suggested, as he had found that iron oxide gave a somewhat different colour.

Professor Ramsay remarked that Stas, in his determination of the ratio of potassium chloride to oxygen in chlorate, had not found that peroxide was formed.

20. "*The Vapour-Density of Hydrogen Fluoride.*" By T. E. Thorpe, F.R.S., and F. J. Hambly.

Gaseous hydrogen fluoride, on being heated from a few degrees above the boiling point of the liquid, shows a rapid decrease in density, owing to the dissociation of H_xF_x molecules ultimately into HF molecules, the course of the dissociation being similar to that observed in the case of nitrogen peroxide and acetic acid. The authors have carefully studied the molecular breaking down of the vapour as it is effected by changes of temperature and pressure. It would appear that there is no evidence for the existence of a molecule corresponding to the formula H_2F_2. If it exists at all, it must be formed only during the process of transition of H_xF_x into x HF, and be such that it can persist under given circumstances only in the presence of definite proportions of molecules more or less complex than itself. The density at above 32° corresponds apparently with H_2F_2, but the curve gives no indication of any condition of statical equilibrium in the neighbourhood of this temperature such as would be manifest if such a molecule were capable of independent existence. At temperatures below this point the density gradually increases in a perfectly regular manner until at 26·4°, the lowest temperature observed, the density becomes 1·773, equivalent to a molecular weight of 51·2 ($H_3F_3 = 60$); as

it is heated the vapour behaves like a mixture of a complex molecule H_xF_x, or of H_xF_x and H_yF_y molecules, with a gradually increasing number of molecules of HF, the process of dissociation being perfectly continuous until the temperature increases to about 60°, when the density becomes approximately normal, *i.e.*, corresponds to a vapour consisting wholly of HF molecules.

As in the case of nitrogen peroxide, dissociation takes place with increasing rapidity as the temperature increases until it attains a maximum when about 50 per cent of the heavier molecules have been decomposed, after which the increase becomes gradually smaller, at first slowly, then rapidly. The curves showing the mean increase resemble in fact that given by Naumann (*Thermochemie*, 1882) as representing the increase in the rate of dissociation of nitrogen peroxide, but with this very marked difference, that the mean increase for 1° C. in the case of hydrogen fluoride is at its maximum nearly three times as great as that of nitrogen peroxide.

The authors have studied the effect of pressure on the course of the dissociation by attenuating a given volume of the gas maintained at the constant temperature of 32°, at which point the vapour is supposed to consist wholly of H_2F_2 molecules. It is seen that the slightest alteration of pressure at this temperature at once disturbs the ultimate proportion of the complex to the simpler molecules in the gaseous mixture—a fact which again points to the non-existence of a stable molecule corresponding to H_2F_2. The reduction of the actual pressure may be effected not on by direct attenuation but by mixing the vapour with a neutral gas. Experiments made by the addition of dry air showed that the intervention of the air particles has no effect on the extent of the ultimate decomposition of the complex hydrogen fluoride molecules corresponding to a particular diminution of pressure. The presence of the air may alter the rate of the dissociation, but it has no appreciable influence on its maximum amount. Lastly, they see in the fact that their values for the density at *circa* 32°, under ordinary atmospheric pressure, agree almost exactly with those obtained by Mallet, a proof that the nature of the vessel or the character of its surface exert no appreciable effect on the extent of the dissociative change, Mallet's experiments having been made in glass coated with paraffin, whereas those of the authors were made in a vessel of platinum. This point is of importance in view of Konowalow's experiments on the effect of surface in influencing the rate and extent of dissociation.

Discussion.

Professor Ramsay said that Professor Thorpe, in speaking of the analogy of the results obtained in the case of hydrogen fluoride with those of the Brothers Natanson for nitric peroxide, had pointed out that these latter afforded insufficient proof of the higher limiting value of n in the formula N_nO_{2n}; and that this limiting value was also unknown in the case of acetic acid, of which the vapour-density also increased with fall of temperature. Now there were three separate lines of argument leading to a knowledge of the higher limiting formulæ of these bodies which had been pointed out by himself and Dr. Young, and of which the data were to be found in papers published in the *Philosophical Transactions*, in the *Philosophical Magazine*, and in the *Chemical Society's Transactions*. The first of these has reference to the alteration of density of the saturated vapour with fall of temperature and corresponding fall of pressure. It is argued that the density of the vapour of a substance must necessarily, at any given temperature, be higher when the vapour is on the point of condensation than when it is unsaturated. Hence, if it can be proved that the density of the saturated vapour of bodies like nitric peroxide and acetic acid shows no signs of increasing beyond those required for the respective formulæ N_2O_4 and $C_4H_8O_4$, such formulæ must denote the limit of complexity of the molecules, in the gaseous state at least. To ascertain such a limit, Dr. Young and the speaker constructed from the Natansons' data for the relations of volume, pressure, and temperature of nitric peroxide, and their own data for the vapour-pressure of that body, isothermal curves in which pressures formed ordinates and vapour-densities abscissæ. The terminal points of such curves are characterised by rapid increase of density without rise of pressure, and, in fact, denote that the substance is no longer in the gaseous state, the vapour-pressure of the liquid having been reached. The densities of the saturated vapour therefore will correspond with the angles of union of the isothermal curves with horizontal straight lines representing condensation to liquid under vapour-pressures constant for each temperature. By joining with each other such angles of union for each temperature a curve is obtained expressing the densities of the *saturated* vapour in relation to pressure. It is evident from inspection of such a curve for acetic acid, shown in a plate in the Society's *Transactions* (1886, 806), that the line of zero-pressure would be cut at the density 60, corresponding to the formula $C_4H_8O_4$; a similar curve can be constructed from the Natansons' results and Ramsay and Young's determinations of the vapour-pressures of nitric peroxide, and this intersects the line of zero-pressure at a point corresponding to the vapour-density 92, equivalent to the formula N_2O_4.

The second argument is as follows:—Representing the relations of temperature and pressure of a "perfect" gas for any given constant volume, $p = c.t$, where c is a constant and t absolute temperature. This is the equation to a straight line; such a line is termed an *isochoric line* or *isochor*, its point of origin for a perfect gas is absolute zero of pressure and temperature. If a different volume be chosen, the slope of the line is different. Now it is clear that if a given volume of gas contains $2n$ mols., pressure will rise with rise of temperature at twice the rate that it would if the given volume of gas contained n molecules. Constructing for nitric peroxide and for acetic acid on the assumption that they are perfect gases diagrams showing the relations of pressure and temperature for the formulæ NO_2 and $C_2H_4O_2$, at such volumes that 1 grm. occupies, say 1000 c.c in each case, the resulting straight lines will manifestly differ in slope from those corresponding to the respective formulæ N_2O_4 and $C_4H_8O_4$, the pressure in the latter case not rising so rapidly with rise of temperature, owing to the smaller number of molecules in that volume. But we know that the actual behaviour of these bodies is not that of perfect gases. The line representing the relations of pressure and temperature should, at high temperatures, when the substances exist in the molecular state NO_2 and $C_2H_4O_2$, nearly coincide with the theoretical line for these molecular states; and at low pressures and temperatures with the line denoting the molecular condition N_2O_4 and $C_4H_8O_4$. The data of actual experiments show that such is the case. The S-shaped isochoric curve trends so that it is probable that it would become tangential with that expressing the behaviour of molecules of the higher formulæ, showing no signs of cutting it, as it must needs do, were still more complex molecules capable of existence.

The third line of argument is derived from the application of Raoult's method to a solution of nitric peroxide in acetic acid; the results obtained by the speaker show that even with very varying proportions of peroxide the molecular weight corresponds closely with the formula N_2O_4.

In conclusion, the speaker suggested that it was very desirable that the authors should, if possible, obtain data for a greater number of isothermals than the two which they had already constructed, so as to afford means for determining the true complexity of the molecule; and also that such results should be checked by the application of Raoult's method, dissolving the hydrogen fluoride in glacial acetic acid.

Professor Thorpe said that it was impossible to apply Raoult's method, on account of the violence of the action which took place on adding hydrogen fluoride to acetic acid.

21. "*Contributions to the Chemistry of Lignification; the Constitution of the Jute Fibre Substance.*" By C. F. Cross and E. J. Bevan.

The authors describe the results of fuller study of the ligno-celluloses (compare *Chem. Soc. Trans.*, 1882, 90; 1883, 18). The substance of the jute fibre may be empirically represented by the formula $C_{12}H_{18}O_9$, and although an aggregate, its properties and composition are sufficiently constant to warrant its being regarded as a chemical unit. It is to a certain extent attacked and dissolved by hydrolytic agents, but the insoluble residues possess the composition and properties of the original; hydrolytic agents which are at the same time oxidising agents, *e.g.*, dilute nitric acid, however, cause its resolution into insoluble cellulose and soluble non-cellulosic acid products. On treatment with a mixture of concentrated nitric and sulphuric acid, it is converted into explosive nitrates, ultimately into what appears to be the tetranitrate, $C_{12}H_{14}O_5(NO_3)_4$.

The characteristic action of chlorine, whereby ligno-cellulose is resolved into cellulose and a yellow chlorinated derivative, has been studied by a special method and apparatus, and it is shown that interaction takes place according to the equation—

$$C_{456}H_{702}O_{342}+24Cl_2 = 6C_{19}H_{17}Cl_4O_9+57C_6H_{10}O_5+3H_2O+24HCl.$$

Previous observations showed the probable presence in the chlorinated fibre of mairo-gallol.

A comparison of the composition of the latter with that of the chlorinated derivative, however, indicates that it is associated with another substance having approximately the formula $C_{137}H_{169}O_{59}$.

Moreover, the chlorinated derivative has been found to contain a constituent yielding, on hydrolysis, furfural and acetic acid. These compounds are also readily yielded by the original ligno-cellulose, and the quantities obtained confirm the empirical formula deduced as above from the statistical comparison with mairo-gallol.

The non-cellulosic constituent therefore appears to be composed of (*a*) a group, $C_{18}H_{18}O_{10}$—a ketone transitional to a quinone, capable of combining directly with chlorine to form mairogallol; (*b*) a furfural group, $C_5H_4O_2$, in combination by condensation with *a* and with (*c*) a group yielding acetic acid. These are associated in the approximate molecular proportions of (*a*) 2, (*b*) 6, (*c*) 5 = $C_{76}H_{80}O_{37}$.

From the examination of various types of lignified tissues and fibres, the authors conclude that the composition of the ligno-celluloses in the earlier stages of growth approximates to that of jute; but that in the true woods, in which the carbon percentage is higher and the properties of which differ sensibly from those of the first named—condensation has proceeded further.

22. "*The Atomic Weight of Chromium.*" By S. G. Rawson, B.Sc.

The author has determined the equivalent of chromium by converting a known weight of carefully purified ammonium bichromate into chromic oxide: the chromate was first reduced by means of alcohol and muriatic acid, an excess of ammonia solution was then added to precipitate the chromium as hydroxide, the water was removed by evaporation, and after drying the residue at 140°, the ammonium salt was expelled by ignition in a muffle. All the operations were carried out in one and the same platinum dish; full details are given in the paper. The results obtained are given in the Table.

Weight of $(NH_4)_2Cr_2O_7$ (corrected).	Weight of Cr_2O_3 (corrected).	Ratio of Cr : H.
1·01275	0·611134	52·130
1·081806	0·65266	52·010
1·29430	0·78090	52·020
1·13966	0·68799	52·129
0·98778	0·59595	52·016
1·14319	0·68987	52·059
General mean		52·061
Maximum difference.. ..		0·120

At the next meeting on March 7th there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Constitution of Certain Naphthalene Derivatives." By Dr. Armstrong and Mr. Wynne.

"The Decomposition of Carbon Bisulphide by Shock." By Professor Thorpe.

NOTICES OF BOOKS.

Chemical Lecture Notes. By P. T. Austen, Ph.D., F.C.S. New York: J. Wiley and Sons.

This book, the author informs us, is not a text-book, but a collection of notes and observations. Some of these observations, especially the glorification of "high" explosives, to be met with in a chapter on "The Chemical Factor in Human Progress," may make us shake our head in doubt, and must at any rate be handed over for appreciation to political, economical, and moral organs. But others, especially the introductory sections, are most valuable. From these sections we are glad to find that in the great war between education and examination Dr. Austen is on our side. He says to the student:—"As your faculties are of use and can be depended on only so far as they have been properly trained and directed, I must satisfy myself that you observe correctly. . . . . You must be on a continual watch that nothing escapes you, and indeed, that your faculties do not deceive you. Whoever causes the mind of pupils to take the necessary action *teaches* the pupils. The teacher is not one who *tells*, but who sets the learner's mind to work. The true method of education is to show you a road by which you cannot help arriving at results for yourselves. The true teacher makes himself unnecessary to the pupil as soon as possible." The road here marked out alike for teacher and student is utterly unlike that followed by the "coach" and for the youth who is preparing for an examination. Dr. Austen further earnestly recommends Herbert Spencer's work on "Education" and Prof. Galloway's "Education, Scientific and Technical."

There is much in this little book which may be most profitably studied.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Mr. J. G. McIntosh (Chemical News, vol. lix., p. 96) will find in the *Journal of the Chemical Society*, 1886, pp. 114—120, that ferrous sulphate *does* absorb ammonia from the soil, &c.

I am afraid he has not read the papers published in the *Journal of the Chemical Society*, 1882—87, with sufficient care, or he would have found that iron sulphate is not only a *direct*, but an *indirect* plant-food.

Concerning Mr. McIntosh's idea of instituting a series of comparative experiments with various sulphates; if he turns to the pages of *La Sucrerie Indigène et Coloniale*,

vol. xxxi., pp. 571—576, he will find that M. Muntz (Professor at the Institut National Agronomique, Paris) says:—"With *any* sulphate there is an increase of 13·54 per cent, but with *iron* sulphate the increase is 30·2 per cent." M. Muntz also obtained an *increase* of 9 6 per cent of chlorophyll in those crops grown with the *iron* manure.

Iron, according to Professor Sachs, is "absolutely necessary for the formation of chlorophyll;" therefore for starch, fat, and woody substances generally. Although our soils contain a certain amount of *iron*, it is not always in the most suitable form for root-absorption, and it may be that many farm crops (which only live a few months) suffer from a want of "this life-giving substance." The weak acids secreted by the rootlets is most likely insufficient to dissolve the requisite amount of iron (from the soil) for a healthy growth.

I think it would be well for Mr. McIntosh to remember that *iron* is an important plant-food, while, on the other hand, *soda* is not a plant-food. I may also remind him that Mr. Yoshida (*Journal of the Chemical Society*, 1887, p. 748) proved the existence of *alumina* in the ashes of the pea, bean, rice, wheat, and cereals generally.—I am, &c.,

"X."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 6, February 11, 1889.

On the Loss of Gaseous Nitrogen during the Decomposition of Organic Matter.—Th. Schlœsing.—The author considers that ammonia is, with nitric acid, the last stage of combination at which the nitrogen of any organic matter may arrive during its decomposition. The ammonia produced in his experiments corresponds to the nitrogenous matters which have ultimately lost all their nitrogen. Consequently, the gaseous nitrogen escaping must be compared with the ammoniacal nitrogen to find the proportion of this gaseous nitrogen lost in the course of the decomposition of the nitrogenous substances. Under the conditions of the author's experiments these losses have been minute. These results seem to clash with those which M. Reiset has obtained, but the author experiments on the destruction of the organic matter, whilst M. Reiset has studied meat and farmyard manure only during the first stage of decomposition. It is quite possible that the loss of nitrogen takes place especially in this stage.

Certain Reactions of the Mercury-ammonium Chlorides.—G. André.—The author studies the decomposing action of water upon the chloramidide with the view of fixing the conditions under which dimercuriammonium is transformed into chloramidide in contact with sal-ammoniac.

On Amorphous Bismuth.—F. Hérard.—Pure crystalline bismuth is heated to full redness in a current of nitrogen; greenish vapours rise up and condense upon the cooler portions as a greyish dust. This dust, if examined under the microscope, appears in the form of minute globes united in links. Such gases as hydrogen and carbon monoxide cannot be used in place of nitrogen in its preparation. The minute sub-division of amorphous bismuth renders it more susceptible to reagents than is crystalline bismuth.

On Titanium Peroxide.—Lucien Lévy.—The author assigns to this oxide the formula TiO_3. It is not an acid in the strict sense of the word.

Syntheses Effected by Means of Cyano-succinic Ether.—L. Barthe.—The author gives an account of methyl-cyanosuccinic ether, of the analogous ethyl compound, of ethylethenyl-tricarbonic ether, and propylcyanosuccinic ether.

Action of Bromine upon Aconitic Acid and Carballylic Acid.—E. Guinochet.—From both these acids the author obtains the same tribromo-compound.

On a Nitrophenol isomeric with Nitro-camphor *a*.—P. Cazeneuve.—The compound obtained has the same percentage composition as nitro-camphor. It is white, and crystallises in long needles with 1 mol. of water of hydration. It is soluble in water, alcohol, ether, and chloroform.

Moniteur Scientifique, Quesneville. January, 1889.

Determination of Phosphoric Acid in Basic Slags.—Dr. M. A. von Reiss (*Zeitschrift angewandte Chemie*).—Among the many methods of dissolving the slag the author prefers the use of hydrochloric acid without separation of the silica. If this separation is necessary in any case he attacks the sample with sulphuric acid at 66° B. The method of analysis which best combines accuracy and dispatch is, he considers, the direct precipitation of the phosphoric acid with magnesia mixture in presence of citric acid. Laubheimer treats the phosphoric solution (freed from silica) containing from 1 to 2 decigrms. of phosphoric acid with 20 c.c. of citric liquid (500 grms. citric acid in 1 litre) and 50 c.c. of ammonia, sp. gr. 0·92. He cools and adds 20 c.c. of magnesia mixture, stirring with a glass rod until the liquid is rendered opaque by the precipitate. The author modifies this process as follows:—He moistens 10 grms. of slag with a little water, adds 50 c.c. of strongest hydrochloric acid, and heats the covered capsule to a boil for some minutes. He removes it from the fire, adds cautiously 50 c.c. of strongest sulphuric acid, and heats until white vapours appear. He then cools for fifteen minutes, takes up in 100 c.c. of water and heats, whilst stirring, until the liquid turns green. If too strong a heat is applied there appears a red precipitate of an iron salt containing phosphoric acid, which does not re-dissolve. The whole is poured into a flask of 500 c.c., and when cold the volume is made up to the mark. Account must be taken of the space taken up by the insoluble precipitate, about 4 c.c. He then adds 4 c.c. of water over and above the 400 c.c., and filters. Of the filtrate he takes 32 c.c. and treats with 10 c.c. of the citric solution and 25 c.c. of ammonia at sp. gr. 0·92. After cooling he adds 25 c.c. of magnesia mixture and stirs. If no immediate turbidity is produced a little more ammonia is carefully added. When the precipitate forms he adds 20 c.c. more ammonia, stirs for a minute, and filters after about ten minutes. The precipitate in its filter is dried and ignited in a porcelain crucible, which is placed first at the mouth of the muffle until the filter is entirely incinerated, and it is then exposed to a bright red heat for an hour.

Determination of Sulphur in Iron.—C. Meinecke (*Zeitschrift angewandte Chemie*).—The author treats 5 grms. of iron, or more if necessary, in a flask with 50 grms. of ammonium copper chloride, 250 c.c. of hot water, and 10 to 15 c.c. of hydrochloric acid. He keeps the whole near the boiling-point until the deposit of copper is re-dissolved, which generally takes place in a quarter of an hour. It is then thrown upon an asbestos filter, washed with hot water acidulated with a little hydrochloric acid, and washed. The contents of the funnel are then transferred into a flask with the smallest possible quantity of water, a few crystals of potassium chlorate are added, about 5 c.c. nitric acid (sp. gr. 1·4), and 10 c.c. hydrochloric acid (sp. gr. 1·19). It is evaporated to dryness in the sand-bath, re-dissolved in a little hydrochloric acid, digesting in heat so as to be sure of having expelled

all the nitric acid, and filtered. In the filtrate the sulphuric acid is determined with barium chloride in the usual manner.

The Avoidance of Tared Filters for Weighing Certain Precipitates.— L. L. de Koninck.— Already noticed.

Determination of Paraffin, Ceresine, or Mineral Oils in Fatty Bodies or Waxes.—F. M. Horn (*Zeitschrift ang. Chemie*).—The author weighs 5 to 6 grms. of the sample in a porcelain dish of 6 to 10 c.m. in diameter, adds 2 to 3 grms. solid caustic potash, 80 c.c. of strong alcohol, and heats in the water-bath whilst stirring. The dried soap formed is passed into a cornet of filter-paper and extracted with chloroform in a suitable apparatus. The chloroformic solution is placed in a tared glass capsule, dried in the water-bath, and then heated for two hours in the stove to 105° to 110°, let cool in the desiccator, and weighed. To determine paraffin in waxes, Horn treats 5 to 6 grms. as above. The mixture of myricic alcohol and paraffin is boiled with acetic anhydride, the myricic alcohol is etherified and dissolves in the acetic acid, whilst the paraffin collects in drops on the surface. The whole is filtered through very compact paper and repeatedly washed first with acetic anhydride and then with hot water. Lastly, the filter is dried at 100° in a precipitating glass, the paraffin is re-dissolved in petroleum ether or chloroform, the solution placed in a tared capsule, evaporated, and the residue is weighed.

Determination of Glycerin in Commercial Glycerins.—R. Benedikt and M. Cantor (*Zeitschrift angewandte Chemie*).—The authors base their process on the principle that glycerin, if boiled with acetic anhydride, is transformed quantitatively into triacetine. If it is then dissolved in water and the free acetic acid is neutralised with caustic soda, we may determine the quantity of dissolved triacetine by saponifying with an excess of standard soda and determining the excess of this reagent by titrating with normal acid. The requisites are:—(1) Hydrochloric acid, hemi-normal or tetra-normal. (2) Dilute soda-lye at 20 grms. caustic per litre. (3) Caustic soda-lye at $\frac{1}{10}$. From 1 to 1·5 grm. of the sample is pladed in a flask holding about 100 c.c., and having a long neck; 7 to 8 grms. of acetic anhydride and 3 grms. anhydrous sodium acetate are added. After boiling for ninety minutes with an ascending condenser it is let cool, 50 c.c. of water are added, and the mixture is again heated to a boil, still using the condenser. When all is dissolved it is filtered into a flask holding 400 to 600 c.c. The filter is washed, and when cold, phenolphthalein is added and the liquid is exactly neutralised with the dilute alkali, stopping before a full red colour is reached. Next, 25 c.c. of the strong alkali are added, taking care to empty the pipette each time exactly in the same manner. The liquid is boiled for thirty minutes, and then the residual free alkali is titrated with normal acid.

Vapour-density of Hydrofluoric Acid. — T. E. Thorpe, F.R.S., and F. J. Hambly.—From the *Journal of the Chemical Society*.

Qualitative Analysis of Colours Fixed upon Woollen Cloth.—Gaston Dommergue.—This paper does not admit of abstraction.

Reclamation of Priority Concerning the Process of M. l'Abbé Godefroy on the "Disinfection" of Alcoholic Phlegms of Hydrogenisation. — Laurent Naudin.—The only notice we can take of this tedious controversy is to protest against the abuse of the word "disinfection," in which M. Naudin indulges.

Results of the Most Recent Analyses of Quinine. —M. Lentz.— From the *Zeitschrift für Analytische Chemie*.

Determination of Carbonic Acid in Atmospheric Air.—G. Lunge and A. Zeckendorf (*Zeit. ang. Chemie*). —The authors make use of an apparatus called a minimeter for forcing the air into a flask of baryta-water.

Industrial Society of Mulhouse, Chemical Section, October 10, 1888.—The chief business of the meeting was the opening of two "sealed papers" which had been deposited by M. St. de Kostanecki, one on a new colouring-matter, nitroso-phenyl-azoresorcine, and the other on the diazo colouring-matters of resorcine.

Meeting of Nov. 14, 1888.

C. Kopp presented a memoir on starch and its derivatives, with especial notice of a product called "universal gum," obtained by treating starch with sulphurous acid under pressure, and at a high temperature.

M. Prud'homme sent in a paper on a spontaneous transformation of dinitro-resorcine.

February, 1889.

Studies on Drying Oils and on Methods for the Analysis of Fatty Bodies.—K. Hasura (*Zeitschrift ang. Chemie*).— This paper does not admit of useful abstraction.

Determination of Salicylic Acid in Beer and Wine (*Zeitschrift angewandte Chemie*).—Rœse founds a process on the following facts:—Salicylic acid dissolves almost entirely in a mixture of equal parts of ether and petroleum ether. Except acetic and carbonic acids, none of the normal acids of beer or wine dissolve in this mixture. On agitating the ethereal liquid with an equal volume of water the acetic acid is eliminated almost entirely. On concentrating the ethereal mixture by evaporation, no ponderable quantity of salicylic acid is lost. The salicylic acid in an aqueous solution may be accurately determined by titration with normal alkali. In the discussion which followed the reading of the author's paper it was shown that salicylic acid present in beer does not disappear in time spontaneously.

New Process for Producing Ammonium Chloride. —A. French.— From the *Journal of the Society of Chemical Industry*.

Manufacture of Aluminium by the Castner Process.

Chinese Treatment of Cobalt Ores.—T. I. Bowler.

The Reductive Action of Hydrogen in Presence of Platinum.—Stephen Cooke.—These three papers are from the Chemical News.

Manufacture of Borax from Boro-natro-calcite.— Dr. Fr. Witting (*Zeit. angewandte Chemie*).—The process consists of the four following stages:—Boiling the mineral with an excess of soda-ash, for half of which bicarbonate may be advantageously substituted; treatment of the mud in a filter-press; crystallisation and treatment of the liquors.

Delta-metal.— Analyses of alloys sold under this name, in which tin ranged from 0 to 19·41 per cent, zinc from 14 to 42, and lead from 0·72 to 6·10. Copper varies from 54 to 60.

"Household Lye" intended as a Substitute for Soap and Soda.—A recent fraud, containing 68 per cent of silica, clay, lime, and magnesia. It is sold by a Heidelberg firm under the name of "ammonine," and is said to contain neither acid nor alkali, but to consist of sulphuretted hydrogen (!) condensed and crystallised. It is said not only to bleach linen, but to destroy vermin, bacteria, &c.

An Associate of Indigo.—M. Bieret.—The author asserts that indo-phenol can be added to an indigo-vat with great economy.

Determination of Sulphur in Coal.—R. Brullé.— The author, instead of a platinum capsule, effects the combustion in a long platinum boat, 0·30 metre in length by 0·015 in width and depth. A ledge along each side

allows the cover to slide longitudinally from end to end, so as always to be over the part which is being heated.

Determination of Invert-Sugar by Means of Cupro-alkaline Solutions.—F. G. Weichmann.—From the *School of Mines Quarterly*.

Determination of Higher Homologous Acids in Artificial Salicylic Acid.—E. E. Ewell and A. B. Prescott.—From the *Pharmaceutical Journal and Transactions*.

MISCELLANEOUS.

The Newly Discovered Aluminous Compounds.—In the note which appeared on the first page of the CHEMICAL NEWS for the 15th instant we accidentally omitted to state that the new double fluoride was obtained by Dr. Hampe, and that the discovery was first published in the *Chemiker Zeitung* (Goethen).

Patent Laws.—Under the title of "The True Position of Patentees," Mr. H. Moy Thomas has published, through Messrs. Simpkin, Marshall, and Co., a little book in which the patent laws and regulations at home, abroad, and in the colonies and dependencies are explained for the information of English inventors.

Determination of Chlorides in Urine.—Brignone (*Annali di Chimica*).—The author prefers a process first devised by Mohr. The sample is evaporated to dryness, incinerated with an addition of permangananate, and the solution in water is titrated with permanganate.

The Loss of Nitrogen during the Decomposition of Organic Matter.—Th. Schlœsing.—The author finds that this question has not been fully decided by the researches of Reiset, of Lawes and Gilbert, and of Kœnig and Morgan. He therefore institutes new experiments which are here described and figured. His results will be given on a subsequent occasion.—*Comptes Rendus*, Vol. cviii., No. 5.

Determination of Caoutchouc in Plants.—G. Kassner (*Archiv. der Pharmacie*).—The plants, dried and powdered, are exhausted with benzene, petroleum ether, or carbon disulphide. The extract is evaporated to dryness and treated with boiling alcohol. The insoluble residue is freed from fats, waxes, and chlorophyll by heating with alcoholic potassa and repeated washing with hot dilute alcohol. The pure caoutchouc thus obtained is an elastic mass, still having a slightly dark colour, and is perfectly soluble in carbon disulphide and chloroform.

An Abridged Method for Determining Potassium in Ashes, Minerals, &c.—M. Kretzschmar (*Chemiker Zeitung*).—Supposing that from 0·5 to 1 grm. of the substance is sufficient for the determination of the potassa, 5 grms. are placed in an Erlenmeyer flask, if possible, in a hydrochloric solution. Any ferrous oxide present is peroxidised by means of a few drops of nitric acid, the sulphuric acid is precipitated at a boil by means of barium chloride, and the liquid, while still hot, is supersaturated with ammonia and ammonium carbonate. The liquid, along with the precipitate, disregarding any traces adhering to the sides of the flask, is transferred to a porcelain capsule, evaporated to dryness on the water-bath, and the whole dried at 110°, stirring twice or thrice. After adding a few drops of ammonia it is redissolved in hot water. The precipitate takes the form of a not very bulky insoluble powder, which can be easily washed. It is made up to 500 c.c., of which from 50 to 100 c.c. are taken for the determination. If the quantity of the magnesia present is trifling, the measured quantity of the liquid is evaporated down at once in a platinum capsule, and after the ammoniacal salts have been expelled and the residue dissolved the potassa is determined. If a considerable quantity of magnesia is present a very tedious washing of the potassium platino-chloride is necessary, on account of the sparing solubility of the magnesium platino-chloride. It is therefore more advantageous to evaporate down the measured quantity of the filtrate with an excess of oxalic acid, and, after faintly igniting the residue and filtering off the magnesia, the filtrate is used for determining the potassa.

Detection and Determination of Small Quantities of Chromic Oxide.—E. Donath and Rud. Jeller.—The solution, containing small quantities of chromic oxide along with an excess of ferric oxide, alumina, manganous oxide, and possibly alkaline earths, is allowed to flow into a hot solution of sodium carbonate mixed with permanganate. After a short ebullition the excess of permanganate is reduced by the addition of a few drops of alcohol and filtered. Ferric oxide, alumina, manganese, and the alkaline earths are precipitated, whilst the chrome remains in solution in the state of chromic acid in the filtrate, which will have a yellowish colour if the quantity of chrome is at all considerable. If the colour is not perceptible and the liquid appears colourless the filtrate is slightly concentrated, acidulated with dilute hydrochloric or sulphuric acid, and a drop of it is applied to a fragment of starch which has been previously moistened with a fresh prepared solution of potassium iodide. The appearance of a violet colour betrays the presence of chromic acid. If the filtrate was perceptibly yellow it gives the well-known iodine reaction on acidulation with hydrochloric acid and addition of potassium iodide and a little carbon disulphide. For the quantitative determination of very small quantities of chrome the authors proceed quite in the same manner, but the solution is dropped slowly from a pipette into the hot alkaline solution of permanganate, and the liquid is heated for ten minutes. The filtrate, after acidulation with hydrochloric acid and the addition of a little alcohol, is heated, and chromium sesquioxide is precipitated in the usual manner with ammonium sulphide.—*Zeitschrift fur Analytische Chemie*, vol. xxviii., Part 1.

Bad Manners in Business.—Under this title Dr. Krause, the editor of the *Chemiker Zeitung*, protests against certain bad customs in correspondence which have lately become prevalent, and which serve for the especial annoyance of editors. The first is the common practice of abridging the names of places, so that the recipient of a letter can only guess its origin. Along with this sin comes that of illegible signature. A third abuse is that some persons, in remitting small sums of money, take it upon themselves to deduct postage and sometimes the cost of post-office orders or postal orders. Next follows the abuse of sending remittances in foreign stamps, which the recipient cannot cash without much trouble. This transgression is rarely practised in Britain. Some correspondents do not prepay their communications sufficiently, and thus put the receiver to needless expense. Dr. Krause further complains of the practice of drying letters, MS., &c., with sand, instead of with blotting-paper. Another abuse mentioned is writing letters in copying-ink and not copying them. Matter intended for the press should, in our opinion, not be written with copying-ink at all. The characters are almost invariably blurred, and the compositor works less rapidly and with less certainty than if ordinary ink had been used. Finally our contemporary adds the recommendation that every one should have his address printed on his envelopes. One addition we must venture to make, that is the recommendation that Germans in all communications outside their own country should use the so-called Latin script as employed in the rest of the civilised world. A foreigner may be able to read, write, and speak the German language with ease and correctness, but to decipher a memoir written in German characters proves often a very heavy tax upon his time and patience.

MEETINGS FOR THE WEEK

Monday, March 4th.—Medical 8.30.
—— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Cider," by Messrs. Higgins and Heron. Discussion—"In what Direction is State Aid Needed to Assist Technical Education in Chemistry."
Tuesday, 5th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Pathological, 8.30.
—— Sanitary Institute, 8. "General History, Principles, and Methods," by Dr. B. W. Richardson, F.R.S.
Wednesday, 6th.—Society of Arts, 8. "Arc Lamps and their Mechanism," by Prof. Silvanus P. Thompson.
—— Geological, 8.
Thursday, 7th.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Royal Society Club, 6.30.
—— Chemical, 8. "Constitution of certain Naphthalene Derivatives," by Dr. Armstrong and Mr. Wynne. The Decomposition of Carbon Disulphide by Shock," by Prof. Thorpe.
Friday, 8th.—Royal Institution, 9. "The Discharge of a Leyden Jar," by Prof. O. Lodge.
—— Medical, 8.30. (Anniversary).
—— Quekett Club, 8.
—— Astronomical, 8.
—— Society of Arts, 8. "Present Condition and Prospects of Indian Agriculture," by Prof. Robert Wallace.
Saturday, 9th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
—— Physical, 3. "On the Magneto-optic Notation by Transient Currents with reference to the Time required for the Production of the Effect;" "On an Electrostatic Field Produced by Varying Magnetic Induction;" "On some Experiments Allied to those of Hertz;" "On the Velocity of Electric Pulses along a Pair of Isolated Wires;" "Sundry Laboratory Notes;" by Prof. O. J. Lodge, F.R.S.

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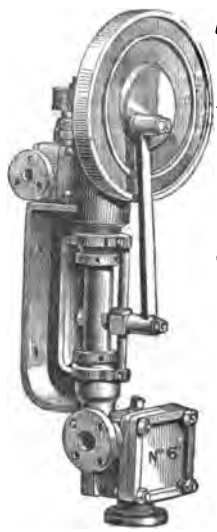

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THE CHEMICAL NEWS.

Vol. LIX. No. 1528.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 104).

Methods for Milk Analysis.

Estimation of Water.

From a weighing-bottle take 5 c.c. milk, put in a weighed thin glass dish or dish lined with tinfoil one-third full of powdered asbestos; dry for two hours at 100° C. The temperature obtained in a boiling water-bath does not reach 100° C. The milk should be dried in an air-bath, the temperature of which is carefully controlled.

Alternate Method of Estimating Water.

Evaporate 1 to 2 grms. of milk in shallow watch-glass or platinum dish on the water-bath for thirty minutes. Dry for an hour at 100° C. and weigh.

Estimation of Casein.

Take 5 grms. of milk, digest in Kjeldahl apparatus with 20 c.c. H_2SO_4, and estimate ammonia in the usual way.

Alternate Method of Estimation of Casein.

Rub up in a mortar the thin disc containing the dried residue from the above process or remove the foil containing it and transfer to soda-lime combustion tube in the usual way.

The mortar and pestle must be well cleaned with the soda-lime, and these cleanings placed in the tube.

Or the dish or tinfoil and its contents may be transferred to a digestion flask and the casein estimated by the method of Kjeldahl.

Estimation of Fat.

Method of Adams.—The kind of paper and the method of using it first proposed by Adams are as follows:—

As for material, the only extra article is some stout white blotting-paper, known in the trade as "white demy blotting, mill 428," weighing 38 pounds per ream. This should be in unfolded sheets, machine-cut into strips 2½ inches wide, and 22 inches long; each sheet in this manner cuts into seven strips.

I have tried other papers but none have answered so well as this; it is very porous and just thick enough. Each of these strips is carefully rolled into a helical coil, for which purpose I use a little machine, made by myself, consisting of a stout double wire, cranked twice at right angles, and mounted in a simple frame. One end of the strip being thrust between the two wires, the handle is turned and the coil made with great facility. This may be done, for the nonce, on a glass rod, the size of a cedar pencil. Two points have to be carefully attended to; the paper must not be broken, and the coil must be somewhat loose, the finished diameter being a little under an inch. I am in the habit of rolling up a considerable number at a time and placing each within a brass ring as it is rolled, inscribing on one corner with a lead-pencil its own proper number.

These coils are next thoroughly dried, and I need hardly say the accuracy of the process depends upon this drying. This can be satisfactorily done in an ordinary air-bath at 100° C., providing the bath be heated properly and the paper kept in it long enough. I found the common way of heating the thin bottom of the bath with a single jet not to answer. My bath is placed upon a stout iron surface, which is heated by a large ring of jets; in this way the heat is evenly distributed over the whole of the bottom of the bath, and the papers, which are put in a cage frame of tinned iron-wire 5 by 2½ inches and divided into eight partitions, get evenly and completely dried, if allowed to remain in the bath all night, and weighed in a weighing-tube next morning, and their weights having been registered according to their numbers, stored away ready for use, as follows:—

The milk to be examined is shaken, and with a pipette 5 c.c. are discharged into a small beaker 2 inches high by 1½ inches in diameter, of a capacity of about 30 c.c., weighing about 12 grms. This charged beaker is first weighed and then a paper coil gently thrust into the milk very nearly to the bottom. In a few minutes the paper sucks up nearly the whole of the milk. The paper is then carefully withdrawn by the dry extremity of the coil and gently reversed and stood, dry end downwards, on a clean sheet of glass. With a little dexterity all but the last fraction of a drop can be removed from the beaker and got on the paper. The beaker is again weighed and the milk taken got by difference. It is of importance to take up the whole of the milk from the beaker, as I am disposed to consider the paper has a selective action, removing the watery constituents of the milk by preference over the fat.

The charged paper is next placed in the water-oven on the glass plate, milk-end upwards, and rough-dried. Mismanagement may possibly cause a drop to pass down through the coil on to the glass. This accident ought never to occur; but if it does it is revealed in a moment by inspection of the surface of the glass, and the experiment is thereby lost.

In about an hour it is rough-dried and in a suitable condition for the extraction of the fat.

The method of Adams has been thoroughly tried by the English chemists and has received the approval of the English Society of Public Analysts. It gives uniformly about 0·2 per cent more fat in normal milk than the ordinary gravimetric methods.

The following modifications of the process may be used:—

The blotting-paper is replaced by thick filtering-paper cut into strips two feet long and 2·5 inches wide. These are thoroughly extracted by ether or petroleum or alcohol.

One end of the strip of paper being held horizontally by a clamp or by an assistant, 5 c.c. milk is run out by a pipette from a weighing-bottle along the middle of the strip of filtering-paper, being careful not to let the milk get too near the ends of the paper, and to secure an even distribution of it over the whole length of the slip. The pipette is replaced in the weighing-bottle and the whole re-weighed, and thus the quantity of milk taken is accurately determined. The strip of paper is now hung up over a sand-bath in an enclosed space, high enough to receive it, where the air has a temperature of 100° C. (*circa*). In two or three minutes the paper is thoroughly dry. It is at once, while still hot, rolled into a coil, and placed, before cooling, in the extraction apparatus already described.

The fat is dissolved by ether or petroleum, collected in a weighed flask, and after thorough drying, weighed.

The fat after extraction may also be estimated volumetrically, as described in the method of Morse.

From data which have been collected, it appears that the estimation of the fat in milk by the lactocrite is strictly comparable with the results of the Adams method. Those who have this instrument, therefore, can use it instead of the method given.

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10 1888.

Alternate Method of Estimating the Fat in Milk.

Method of Morse, Piggot, and Burton.—This method consists in the dehydration of the milk by means of anhydrous sulphate of copper; the extraction of the fat by means of the low-boiling products of petroleum; the saponification of the butter by means of an excess of a standard solution of potassium hydroxide in alcohol; and the determination of the excess of the alkali by means of a solution of hydrochloric acid. The following apparatus and reagents are required:—

1. A porcelain mortar and pestle.
2. An extraction tube, 14 or 15 m.m. in diameter, 220 m.m. in length, with funnel-shaped top. A straight chloride of calcium tube may be used for this.
3. A 200 c.c. Erlenmeyer flask, strong enough to be used with a filter-pump.
4. A suitable stand for holding the flask and extraction-tube.
5. Ten c.c. pipettes.
6. Weighing-glasses with ground-glass stoppers.
7. A low-boiling gasoline, distilling between 30° and 0° C.
8. Dehydrated sulphate of copper.
9. Semi-normal solution of potash in 95 per cent alcohol.
10. A semi-normal solution of hydrochloric acid.

Manipulation.—Place about 20 grms. of the anhydrous copper sulphate, roughly measured in a copper spoon of the size to hold about that amount, in a porcelain mortar; make a cavity in the centre of the mass with the pestle. Allow 10 c.c. of the milk to run on to the copper sulphate, being careful that none of it touches the sides of the mortar. When the milk is nearly dry, grind the mass up with a little clean sand, transfer to the extraction-tube, gently pressing it down in the tube by means of a glass rod. The lower portion of the extraction-tube to be packed with clean cotton-wool. The fat is extracted in the following way:—15 c.c. of benzine are poured over the material in the extraction-tube and drawn down, with the aid of the filter-pump, until the whole of the mass to be extracted has become wet with the liquid, when the connection with the pump is closed; after about five minutes another portion of 15 c.c. of benzine is poured into the tube and the whole of the liquid slowly drawn through with aid of the pump into the flask. Usually one extraction of this kind is sufficient to withdraw the whole of the butter, but for the sake of greater accuracy the process may be repeated two or three times.

Titration.—The benzine may be evaporated and the residual butter fat saponified with about 25 c.c. of the approximately semi-normal potash. The residual alkali is determined by means of the semi-normal hydrochloric acid, using phenol-phthalein as indicator. The difference between the amount required in this process and the amount necessary to neutralise the quantity of alkali taken gives the amount of alkali required for the saponification. The number of m.grms. of potash required for one grm. of the fat is taken at 230. The fat may also be accurately titrated without evaporating the benzine.

Alternate Method of Estimating Water and Fat in Milk.

Method of Babcock.—In the bottom of a perforated test-tube is placed a clump of clean cotton; the tube is then filled three-quarters full of ignited asbestos, lightly packed, and a plug of cotton inserted over it. The tube and contents are weighed and the plug of cotton carefully removed and 5 grms. of milk from a weighed pipette run into it, and the plug of cotton replaced. The tube connected at its lower end by a rubber tube and adapter with a filter-pump is placed in a drying-oven of 100° C., and a slow current of dry air drawn through it until the water is completely expelled, which in no case requires more than two hours.

The tube containing the solids from the above operation is placed in an extraction apparatus and exhausted with ether in the usual way.

Alternate Method of Estimating Water and Fat.

Method of Professor Macfarlane.—A glass tube 4 to 5 c.c. in length and 2 c.m. in diameter, open at one end, drawn out to a tube 5 m.m in diameter at the other end, is two-thirds filled with asbestos fibre, such as is used in manufacturing packing. It is dried in the water-bath for several hours, cooled in the desiccator, and weighed. Ten c.c. of the milk is then added from a pipette, which is completely absorbed by the asbestos. It is then weighed, the additional weight of the milk representing the amount taken. The tube, along with many others, is placed in a water-bath with constant level and dried for ten or twelve hours (during the night) at a temperature of 90°. Next morning the tubes are cooled in the desiccator and weighed, the loss in weight being the moisture. The tubes are then placed in the Soxhlet extraction apparatus and exhausted with petroleum ether for four hours. They are then removed and dried in a steam-bath, cooled in desiccator, and weighed. The loss represents the butter fat.

The Estimation of Sugar.

The reagents, apparatus, and manipulation necessary to give the most reliable results in milk-sugar estimation are as follows:—

Reagents.—1. *Basic Plumbic Acetate,* specific gravity 1·97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One c.c. of this will precipitate the albumens in 50 to 60 c.c. of milk.

2. *Acid Mercuric Nitrate.*—Dissolve mercury in double its weight of nitric acid, specific gravity 1·42. Add to the solution an equal volume of water. One c.c. of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric Iodide with Acetic Acid.*—KI 33·2 grms., $HgCl_2$ 13·5 grms., H,C_2H_3O 20 c.c., H_2O 64 c.c.

Apparatus.—(1). Pipettes marked at 59·5, 60, and 60·5 c.c. (2). Sugar flasks marked at 102·4 c.c. (3). Filters, observation tubes, and polariscope. (4). Specific gravity spindle and cylinder. (5). Thermometers.

Manipulation.—(1). The room and milk should be kept at a constant temperature. It is not important that the temperature should be any given degree. The work can be carried on equally well at 15° C., 20° C., or 25° C. The slight variations in rotary power within the above limits will not affect the results for analytical purposes. The temperature selected should be the one which is most easily kept constant.

(2). The specific gravity of the milk is determined. For general work this is done by a delicate specific gravity spindle. Where greater accuracy is required, use specific gravity flask.

(3). If the specific gravity be 1·026, or nearly so, measure out 60·5 c.c. into the sugar flask. Add 1 c.c. of mercuric nitrate solution, or 30 c.c. mercuric iodide solution, and fill to 102·4 c.c. mark. The precipitated albumen occupies a volume of about 2·44 c.c. Hence the milk solution is really 100 c.c. If the specific gravity is 1·030, use 60 c.c. of milk. If specific gravity is 1·034, use 59·5 c.c. of milk.

(4). Fill up to mark in 102·4 c.c. flask, shake well, filter, and polarise.

Notes.—In the above method of analysis the specific rotatory power of milk-sugar is taken at 52·5, and the weight of it in 100 c.c. solution to read 100 degrees in the cane-sugar scale at 20·56 grms. This is for instruments requiring 16·19 grms. sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk-sugar, whatever instrument is employed.

Since the quantity of milk taken is three times 20·56 grms., the polariscopic readings divided by 3 give at once the percentage of milk-sugar when a 200 m.m. tube is used.

If a 400 m.m. tube is employed, divide reading by 6; if a 500 m.m. tube is used divide by 7·5.

Since it requires but little more time, it is advisable to make the analysis in duplicate and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102·4 for 60 c.c. no correction for volume of precipitated caseine need be made. In no case is it necessary to heat the sample before polarising.

In the above method no account is taken of the fat which is retained on the filter with the caseine. It is worth while to enquire if a correction similar to that made for the albumenoids should not also be made for the fat? (See *ante*, Vieth's Investigation of this subject from *Analyst*, xiii., 63).

Estimation of Ash.

Evaporate to dryness in a weighed platinum dish 20 c.c. of milk from a weighing-bottle, to which 6 c.c. of HNO_3 has been added, and burn in muffle at low red heat until ash is free from carbon.

(To be continued).

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.*

By FRANK AUSTIN GOOCH and JAMES EDWARD WHITFIELD.

Introduction.

The series of waters—forty-three in all—of which it is the purpose of this paper to give some account comprises typical representatives of the geysers, hot springs, mud springs, cold springs, and surface waters found within the limits of the Yellowstone Park. It embraces collections made during the field seasons from 1883 to 1886 under the direction of Mr. Arnold Hague, geologist in charge of the Yellowstone Park Division, and submitted to us for analysis. In our account we have to deal simply with the results of analysis and with the analytical processes we have used—with the latter on the ground that some knowledge of the methods employed in the examination and of the quantities of material at our disposal is essential to a correct understanding of the meaning and value of the analyses themselves. Discussions of the broader chemical aspects of the problems which are involved in a thorough consideration of the relations of these waters, of correlative matters of geological interest, and of the physical phenomena belong properly to others.

The difficulties in the way collecting and transporting large quantities of water in a region comparatively inaccessible were such that the number of large samples, for the more complete analyses, was restricted to a half-dozen; but, though at the beginning of the examination it was supposed that a partial analysis, such as might be made with smaller amounts of material, must suffice, it happened, fortunately, that the development of certain methods as the work progressed has so far extended the reach of the analyses of the smaller samples that from them it is possible to deduce results of fair accuracy, and, if such elements be left out of consideration as are shown by the more elaborate analysis to be present either not at all or only as traces in closely comparable waters, nearly as comprehensive results as those drawn from the examination of the larger samples.

Operations in the Field.

The examination of the waters was necessarily confined in the field to a very few points. Note was made of the *clearness* or *turbidity*, the *reaction* to litmus and turmeric, the *temperature*, and the presence or absence of *hydrogen sulphide*. The tests for the last were the sense of smell and the action of the water upon a polished silver blade.

The operations of collecting and preparing the samples for transportation were carried out as simply as possible. The water was bottled in boxed demijohns when it was possible, and otherwise in beer bottles. In every case great care was taken to clean the receptacle thoroughly and rinse before bottling with some of the water to be examined. In the greater number of cases the waters were so marvellously clear that filtration was entirely superfluous. When, however, the need and opportunity occurred the waters were filtered previous to bottling. All samples were corked tightly and sealed hermetically.

The size of the sample varied from a half litre to one hundred litres, according to the purpose for which it was taken; but the great bulk of the largest samples was, in every case excepting one, reduced greatly by the evaporation of the main portion of the sample previous to bottling. In the one exceptional case the sample was taken for the specific purpose of examining it as to its contents in the heavy metals, and was kept for subsequent reduction in porcelain in the laboratory, in order that the danger of contamination by the tin or copper of the tin-lined still which was employed to effect the reduction in the field might be precluded. No attempt was made to fix with more than a rough approximation the quantities of water evaporated. The concentrated waters, with the rinsings of the still in the natural water of the charge (such portions of the residue as adhered to the walls of the vessel having been dislodged as completely as possible by gentle friction with a rubber or the ball of the finger), were carefully bottled and sealed, and the determination of the degree of concentration was left to be effected in the laboratory in a manner to be described later. A portion of the water represented by the concentrated sample was always reserved in the natural condition for examination.

For the determination of hydrogen sulphide special samples of from 600 c.m.^{3} to 700 c.m.^{3} were generally taken, and to each, if the water did not carry free sulphur, was added before corking and sealing a small amount of lead acetate in crystals. Doubtless it might have been well to fix the hydrogen sulphide similarly in the case of waters carrying free sulphur, having first separated this by filtration; but on the few occasions when that need arose the means of removing the sulphur were not at hand. In these cases, therefore, the samples were simply bottled and sealed with care, and kept for examination in the laboratory.

Nearly all the waters examined were hot when the samples were taken and not surcharged with carbonic acid. It was considered unnecessary, therefore, under the circumstances, to take a special sample for the determination of the carbonic acid and treat it in the field so as to fix that gas in insoluble form, but for this estimation reliance was placed upon the general sample which, as has been said, was corked and sealed with great care.

Operations in the Laboratory.

The operations in the laboratory comprised the determination of the specific gravity of the waters and, in the concentrated samples at hand, the estimation of the substances given in Table (see next page).

In analyses for which the natural water alone was available those substances only were sought which are marked in the table with an asterisk (*).

The determination of what is known as the *total residue*, the amount of solid matter left upon evaporating a known amount of water, is usually regarded as desirable, if for no other reason than to serve as a control of the summation of the determinations of the individual constituents; but the complexity of these waters and the relations of the combined salts are such that it is not possible to

* *Bulletin of the United States Geological Survey*, No. 47.

*Silicic acid.	*Arsenic.
Titanic acid.	Antimony.
*Sulphuric acid.	*Iron.
Sulphurous acid.	*Aluminum.
*Carbonic acid.	Manganese.
Nitric acid.	Barium.
Nitrous acid.	Strontium.
Phosphoric acid.	*Calcium.
*Boric acid.	*Magnesium.
*Chlorine.	Cæsium.
Bromine.	Rubidium.
Iodine.	*Potassium.
Fluorine.	*Sodium.
*Sulphur.	*Lithium.
*Hydrogen sulphide.	*Ammonia.
Copper.	*Albumenoid ammonia.
Lead.	

arrive at the same end in two successive treatments by evaporation and desiccation of the residue. The action of free silica, which is an abundant constituent of the waters, is to set free during the process carbonic acid from the carbonates and boric acid from the borates; to magnify the tendency of the chlorides of calcium, magnesium, and lithium to exchange chlorine for oxygen, and, if the temperatures be pushed sufficiently high, to dehydrate the silica and to volatilise sulphuric acid. Furthermore, the extent of such action is variable and indeterminate. There is obvious reason, therefore, for the difficulty which we experienced in obtaining residues of constant composition; and similar obstacles, as we found practically, oppose the attempt to reduce the residue to a definite condition by evaporation and ignition with sulphuric acid in excess. By means of no device which occurred to us (and several lines of experimentation which need not be mentioned here were followed) were we able to apply, in any form, this general method of control. The proof of the accuracy of our analytical work rests, therefore, upon the agreement of duplicate determinations.

For convenience in the matter of arrangement, we describe first those methods of analysis which were applied to waters in the natural condition; and the account of the treatment of concentrated waters follows. Methods for the determination of certain substances are described under both heads. For when the entire work was done upon the natural water the mode of examination was sometimes made, of necessity, by processes different from those which were applied in the examination of concentrated water; and under reversed conditions the converse was true. In some of the earlier analyses methods were employed which later experience taught us might be advantageously replaced by processes which were developed subsequently. In the account of the methods employed all of these are placed under the proper head; and in the statement of analyses mention is made when there might be doubt of the particular method adopted.

Treatment of Natural Waters.

Specific Gravity.—The figures which stand for the specific gravity of a water represent the weight of any volume of the water under consideration at 15·5° C. compared with the weight of the same volume of distilled water at the same temperature. The determinations were nearly all made with a Geissler bottle, fitted with a ground tubular stopper and cap, and a thermometer. In a few of the earlier determinations a bulb-apparatus similar in general principle, but wanting the immersed thermometer, was employed. The temperature of the water in the bottle was taken immediately after the final adjustment of volume, and the latter was effected instantly and without handling after the filled bottle had been permitted to stand a few moments to bring about an equal distribution of temperature. When the bulb-apparatus was employed the temperature of the water was taken before filling the bulb and after weighing, and the mean of the two readings was assumed to be the temperature of the water at the time when the volume was adjusted. The weight shown by the balance was taken as the weight of the water which would fill the apparatus at the temperature noted. The weight of the same volume of the water at 15·5° C. was calculated from the weight observed, upon the assumption that the coefficient of expansion of the water under examination was the same as that of pure water. The rates of the value thus found to the value found by a similar treatment of pure water is a specific gravity at 15·5° C. It is obvious that, in order that the assumption of the identity of the coefficients of expansion of the water under examination and of pure water may be the occasion of the least error, the observed temperature must be as near 15·5° C. as may be; and that the temperature of the balance-room should be not far from the same, in order that errors which may arise from changes of temperature in the water during the manipulation and from the establishment of air-currents in the balance-case may be less liable to occur. So far as we were able these sources of inaccuracy were guarded against, but the conditions under which the work was performed necessitated the application of corrections rather greater than we should wish. The figures which represent the specific gravity in the statement of the analyses are probably not accurate beyond the fourth decimal place.

Hydrogen Sulphide and Free Sulphur.—Hydrogen sulphide in waters which did not carry free sulphur was determined in the special sample to which lead acetate had been added in crystals at the time of bottling. Before breaking the seal of the bottle a scratch was made upon the neck on the line of the meniscus of the water within, and the volume of the sample—usually about 600 c.m.³—was determined subsequently with sufficient accuracy (the amount of hydrogen sulphide present being always trifling) by finding the volume of water necessary to fill the bottle to the mark. The precipitate which had been formed in the bottle by the addition of lead acetate was left undisturbed at first, and the supernatant liquid decanted as completely as possible. Then the precipitate was easily removed, and for the most part dissolved by means of a little sodium hydrate in solution, and the solution and remaining precipitate were added to the water previously decanted. At this point the lead sulphide showed itself, if any was present, and was collected without difficulty by filtering the alkaline liquid in which it floated through a felt of asbestos in a perforated crucible, in the manner described by one of us previously.* The felt and the adherent precipitate were transferred to a beaker, treated with potassium chlorate and hydrochloric acid to oxidise the sulphide, and the sulphuric acid thus formed was determined by precipitation as barium sulphate. From waters carrying free sulphur that element was separated by filtration. The residue, after washing sufficiently to remove the sulphates, was treated with hydrochloric acid and potassium chlorate, and the resulting sulphuric acid was determined as barium sulphate. The filtrate from the sulphur contained the hydrogen sulphide, if it was present in the sample, and this was removed by lead acetate and estimated in the manner described above.

Sulphurous Acid.—The test for sulphurous acid was made in the case of a few waters which did not carry more than a trace of hydric sulphide by titrating 200 c.m.³ of the water, acidified with sulphuric acid, with a standardised solution of potassium permanganate. In none of these was a reducing action found greater than was attributable to the action of the hydrogen sulphide and arsenic (assumed to be in the condition of arsenious acid) known to be present.

Sulphuric Acid.—The sulphuric acid was precipitated from a known weight of water, after acidifying distinctly with hydrochloric acid and heating to boiling by means of barium chloride. After cooling and settling, usually after twelve hours, the supernatant liquid was decanted as com-

* *Am. Chem. Jour.*, vol. i, 1879. p. 327.

pletely as possible from the precipitate and passed through an asbestos felt in a perforated crucible. The precipitate remaining in the beaker was boiled with a small portion of strong hydrochloric acid, and the latter was removed by evaporation on the water-bath. Treatment with hot acidulated water left the precipitate as pure as barium sulphate may be, and ready for collection upon the same felt through which the supernatant liquid had been poured. Thorough washing, ignition, and weighing completed the operation.

Nitric and Nitrous Acids.—In examining the waters as regards their contents in nitric and in nitrous acids a modification of the indigo method was followed. The action of these acids upon indigo is known not only to be variable with the conditions of dilution, temperature, and the proportion of sulphuric acid added, but also to be dependent upon the order in which the solution of indigo, the sulphuric acid, and the nitrous or nitric acid are intermixed. On this account great care was taken to secure uniformity of treatment of the standard solutions and the water under the test. For preliminary testing a portion of water was reduced by evaporation to a volume of 50 c.m.³ cooled to the temperature of the air, introduced into an Erlenmeyer flask, and mixed with an equal volume of strong sulphuric acid. To the mixture the solution of indigo was added until a distinct tinge of green became visible. In this manner the amount of the solution of indigo from which a given amount of the water under test would discharge the colour became known approximately. For the exact test the portion of water, after evaporation and cooling, was brought to a volume which was less than 50 c.m.³ by an amount equivalent to the volume of the solution of indigo used in the preliminary test. To the portion thus prepared were added 50 c.m.³ of strong sulphuric acid at once, and the solution of indigo as rapidly as the catching of the exact point at which the tinge of green appeared would permit. At the instant of colouration the flask with its contents was placed in a bath of paraffin heated to 140° C. The volume of the solution of indigo which had been added was noted, and if at the end of five minutes' heating in the bath the tinge of colour was still visible, this volume was taken as the measure of the nitrates and nitrites in the water. If, on the other hand, the colour vanished during the heating, it was reproduced by the addition of more indigo, and the digestion in the bath at 140° C. was prolonged during another interval of five minutes.

This mode of treatment was repeated until the colouration was permanent during the interval of digestion. The total volume of the solution of indigo employed was recorded, and its value in terms of nitric acid determined in the manner to be described.

As Warington has shown,* the oxidising power of nitric acid upon indigo decreases as the dilution of the solution in which the action takes place increases. It is plain, therefore, that in order that the exact value of the volume of the indigo solution employed in the test may be known, the amount of nitric acid needed to discharge the colour from an equal amount of the same solution under the conditions of the test must be determined. To effect this determination we made use of a solution of potassium nitrate of known strength, and found by experiment the amount of it which, mixed with 50 c.m.³ of strong sulphuric acid, with water enough to bring the final volume to 100 c.m.³, and with the amount of the solution of indigo employed in the test, was just adequate to discharge all colour excepting the faint characteristic tinge which must remain unchanged after five minutes' heating. The oxidising power of the nitrates and nitrites in the water is exactly measured by the amount of nitric acid in the quantity of the standard nitrate solution which is required to produce the end-reaction. The solution of potassium nitrate which we used contained 0·0001 g. to 1 c.m.³ The mode of manipulation which we adopted keeps the proportion of strong sulphuric acid added to the mixture (excepting the preliminary tests) always the same, and consequently the heat generated in the reaction is the same always. The order in which the reagents are brought together is the same in all cases, and sources of inaccuracy due to the variability of the action of nitric acid with the degree of dilution are eliminated.

(To be continued).

* *Jour. Chem. Soc.*, London, 1879, p. 578.

ON THE

TRUE FORMULA FOR PERMANGANATES.*

By CHARLES M. BRADBURY, of Virginia.

Introductory Note.

THE material obtained by fusing alkali and peroxide o manganese together, which was investigated by Scheele about 1740, and named by him "mineral chameleon," had, as is well known, been observed nearly a hundred years before by Glauber. Up to the early part of the present century, however, but little was known as to its chemical constitution. In 1817 Chevillot and Edwards examined this subject with considerable care,† and concluded that mineral chameleon contained a peculiar acid of manganese, but they did not assign to this proposed acid any formula, nor did they recognise the fact (afterwards ascertained by Forchammer) that they were dealing with two acids of manganese instead of one. The first reliable quantitative analyses of these acids were made in 1832 by Mitscherlich,‡ who assigned to them the respective formulæ that (if we translate from the old to the new chemistry) have been nearly always accepted until very recently. His conclusions have not, however, been unchallenged. Schönbein in 1848 endeavoured to show that permanganates are properly compounds of manganese dioxide with a tetroxide of the base;§ and in 1859 Phipson denied the existence of permanganic acid, while allowing that of manganic.‖

Chemical literature from 1832 to 1835 inclusive contains many discussions on the permanganates; they are again frequently noticed from 1851 to 1856; and from 1859, when their usefulness as disinfectants was pointed out, they have continued to attract attention and to increase in variety of application.

Since the establishment of the new system of chemical nomenclature, and until quite recently, permanganic acid has been almost universally regarded as dibasic, so that the permanganates have been represented as $\overset{I}{R_2}Mn_2O_8$ or $\overset{I}{R}Mn_2O_8$. Some of the newest treatises¶ have, however, substituted for this expression one indicating just half its molecular weight, *i.e.*, $\overset{I}{R}MnO_4$ or $\overset{I}{R}(MnO_4)_2$, without giving any reason for so doing. It was to determine, if possible, whether this change was justified by the facts in the case, that the present inquiry was undertaken.

Is Permanganic Acid Dibasic.

In searching for the correct answer to this question it will be well to examine in the first place the facts that seem to favour the affirmative.

Let us take, for the sake of convenience, potassium permanganate as a type of the entire class. Then, so far as the manner of writing the formula is concerned, it may

* Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)_n$.

† *Ann. de Chim. et de Phys.* (2), iv., 287; also viii., 237.

‡ *Ann. der Chem. und Pharm.*, ii., 10.

§ L. Gmelin, *Handbook of Chemistry*, tr. by H. Watts, iv., 213.

‖ *Comptes Rendus*, l., 694.

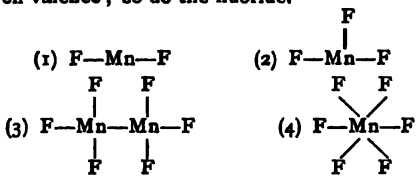
¶ See, for example, Richter's *Inorganic Chemistry* (Dr. E. F Smith's trans.), 1883; *Principles of Chemistry*, M. M. Pattison Muir 1884; *Treatise on Chemistry*, Roscoe and Schorlemmer, 1886

be remarked that under the old system of atomic weights no simpler formula than the one we now write, $K_2Mn_2O_8$, was possible; for K_2O was KO, and permanganate of potash was $KOMn_2O_7$,* or, according to Berzelius, $KOMnO_7$. But inasmuch as the adoption of the new system has resulted in halving the formulæ of many compounds, *e.g.*, nitric acid, which before were in a precisely similar condition, this fact, taken alone, has no greater weight than attaches to the mere priority of the dibasic formula, which is scarcely worthy of mention.

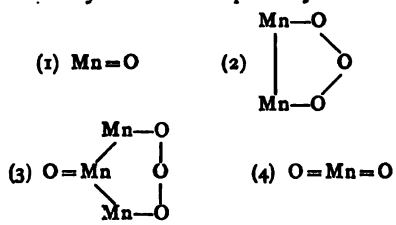
In the second place, however, there is what seems to be a very good reason indeed for retaining the formula $K_2Mn_2O_8$, namely, that manganese undoubtedly deports itself in many cases as an artiad† element, and hence to write potassium permanganate $KMnO_4$ is to violate Gerhardt's law of even numbers. Without giving to this law greater credence than is proper, the fact that it holds in most cases is hardly deniable. Unless good reasons can be shown for disregarding it, it should be observed in this instance.

A few examples of the even valence of manganese will help to show the weight of the evidence in favour of the formula $K_2Mn_2O_8$.

The manganous and manganic chlorides both display this even valence; so do the fluoride.

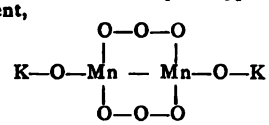


The oxides best known are MnO, Mn_2O_3, Mn_3O_4, and MnO_2, which may be written respectively—

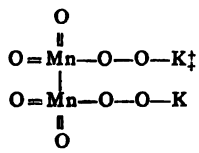


According to the law that quantivalence always varies, if at all, by *pairs* of equivalents, such evidence as the above would seem to prove conclusively that manganese is artiad in all of its compounds.

It is evident that by retaining the molecular formula $K_2Mn_2O_8$ not only is Gerhardt's law satisfied, but it becomes easy enouth to write structural formulæ of probable correctness. For example, supposing manganese to be tetravalent,



or, as is more usual, making it hexavalent,



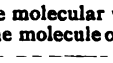
So far as I have been able to discover, the facts just stated—namely, the even valence of manganese taken in connection with Gerhardt's law, and the impossibility, in view of this even valence, of writing a graphic formula corresponding to $KMnO_4$—have determined the retention of the molecular formula $K_2Mn_2O_8$ so long after other apparently double formulæ have been simplified. It is clear that with the nitrates, chlorates, perchlorates, &c., neither of the reasons exist for retaining the double formula that seem to make that course necessary with the permanganates; for the nitrogen and chlorine of these salts, and the elements that bear similar relations to others whose molecular weights have been divided by two since the introduction of the new system, are perissad.

If, then, the dibasic formula corresponds so well with known facts, why should it be called into question, much less rejected? A general answer to this may be found without much difficulty. Stated briefly, it may be divided into two propositions: First, there has been up to the present time *no positive evidence* of dibasicity in permanganic acid in the shape of acid or double salts. Second, there are theoretical considerations, partly of recent development, that permit and, indeed, require the use of the monobasic formula. In other words, at least one of the two laws that indicate so positively the correctness of the old formula must, in the light of later research, be accepted in a modified sense only.

With regard to the first proposition, it is clear that it could hardly be true of a really dibasic acid as well known as permanganic. That in all the experimental study of the permanganates that has been made in the past,* this particular question could, by an accidental coincidence, have been entirely overlooked is highly improbable. In fact, there is one acid permanganate—that of barium—spoken of in one of the older treatises,† but, as will be shown, this fact increases the improbability just alluded to. If even this one acid permanganate could be proved to exist, further discussion as to the basicity of the acid would be unreasonable; but the whole account of it is indefinite, improbable, and contradictory, and recent works do not speak of it at all.

It appears that, according to some observers, if aqueous permanganic acid (obtained by treating a solution of barium permanganate with sulphuric acid) be evaporated at a gentle heat till quite concentrated, it deposits on cooling "dark carmine-red needles, which yield 8·411 per cent of water." This is certainly singular, to say the least, when compared with the admitted fact that a similar solution evaporated over oil of vitriol merely deposits hydrated peroxide of manganese. But without denying that such crystals have been obtained, the question as to what they were is an open one, for Fromherz regarded them, not as acid barium permanganate, but as crystallised permanganic acid. Mitscherlich and Wöhler are said to have inclined to the opinion that they were acid barium permanganate. It does not appear, however, from the account given that any analysis of the crystals had been made, and it is difficult to see how, after enough sulphuric acid had been added to precipitate all the barium and the solution decanted, enough barium could still remain in solution to form an essential constituent of "dark carmine-red needles," or of anything else at all noticeable.

Besides this, the percentage of water given is about three times as much as acid barium permanganate would contain. For assuming that the acid is dibasic and acid barium permanganate possible, it must be,—



or $H_2Ba(Mn_2O_8)_2$, the molecular weight of which is 615. It could yield only one molecule of water, and $\frac{18}{615} = 0{\cdot}029$.

* See, for instance, analysis by Machuca (*Comp. Rend.*, li., 140).

† With regard to the whole subject of quantivalence, I have endeavoured to follow what seem to be the prevailing ideas, as exemplified in Odling's article, "Metals, atomic weights and classification of," in "Watts' Dictionary."

‡ From "Watts' Dict.," 1st Supp., 236.

* See, for instance, an account by Gorgeu (*Comptes Rendus*, l., 610) of a "manganate and permanganate," (?) $Mn_2O_7K_2O.2MnO_2K_2O$.

† Gmelin's *Handbook*, iv., 210.

That the excess could be water of crystallisation is unlikely, whether the substance be compared with other acid salts or with other permanganates; nor is any allusion made to the excess, nor any explanation offered. Finally, attempts to make this "acid barium permanganate" met with no success. Of this more will be said in another place.

The assertion that the dibasic formula has not been supported by *experimental* evidence is, then, justifiable. It will now be shown that the *theoretical* defences of this formula must give way to known facts.

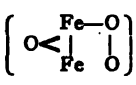
It will suffice for my present purpose to speak of the statement that is the very keystone of the supports of the double formula; namely, that manganese is an artiad element. The evidence in favour of this conclusion is too strong to be set aside without exceedingly good reasons. There is no doubt that in general this element has an even number of atomicities.

If, however, it can be proven that there are exceptions to the rule—that the statement in question, while generally true, is not rigidly so—the *possibility* of the monobasic formula for permanganates will be established.

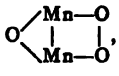
As a matter of fact, while manganese is most frequently of even valence, it can nevertheless exist in a state that (unless the meaning of "valence" be modified, as some have proposed) can only be described as one of uneven or perissad valence. There is ample evidence to prove that the law that quantivalence always varies by twos, while it very generally holds good, does not always do so. The fact that mercury appears to be both monad and dyad is well known; nitrogen also is frequently recognised as peris-artiad. That tungsten does not conform to the law is evident from the list of chlorides of that metal,

$$WCl_2,\ WCl_4,\ WCl_5,\ WCl_6.$$

The same is true of vanadium, which forms the series of chlorides VCl_2, VCl_3, VCl_4, and the oxides V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.* According to Odling,† iron, which is dyad in ferrous oxide (Fe=O), is triad in the ferric oxide—



and similar differences exist in the salts of the allied metals nickel, copper, cobalt, and manganese. This would make graphic formula for Mn_2O_3,—



nstead of that given above. Without accepting even Odling's views with regard to the iron metals (including manganese) as decisive, no reasonable doubt remains that either there are genuine exceptions to the law under discussion, or the meaning of "valence" must be restricted so as to exclude some of the phenomena usually designated by that word. In the present instance it can make no difference which alternative is chosen; it will be sufficient to show that manganese is as much an exception to the law as any other element.

As evidence to this effect, it is fair to mention the fact that some eminent authorities, as Odling, have come to this conclusion by observing the analogy (1) between aluminic and ferric and (2) between ferric and manganic oxides.

Again, although the supposed heptachloride of manganese of Dumas turned out to be an oxychloride, the formula MnO_2Cl_2, assigned to it by H. Rose,‡ in which the manganese is perhaps most naturally regarded as hexad, had been changed by Roscoe§ to MnO_3Cl, and no structural formula can be written corresponding to this, without making the manganese heptad, or at least a perissad of some sort.*

These reasons for regarding manganese as peris-artiad may not be conclusive, but are worthy of attention. Strong and direct evidence may be obtained, however, by a consideration of the *periodic relations* of the element.

(To be continued).

* Roscoe and Schorlemmer, "Treatise," II, ii., 293, 283.
† "Watts' Dict." III, 595 sq.
‡ "Watts, Dict.," 1st Supp., 246.
§ R. and S., "Treatise," II, ii., 22.

* According to Lossen's system (Muir's *Principles of Chemistry*) this statement does not hold good but according to most authorities it does.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

February 23, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MR. M. H. KILGOUR was elected a Member of the Society.

Dr. J. W. WAGHORNE read a "*Note on the Measurement of Electrical Resistance*," showing that two resistances may be compared by joining them in series with a battery, and observing the deflections of a galvanometer connected successively with their terminals. The resistances are proportional to the currents which pass through the galvanometer in the two cases, provided they are large compared with that of the battery, or are not very different from each other. By using a rocking key the method is rendered expeditious, and the galvanometer resistance need not be known.

"*On a New Polarimeter*," by Prof. S. P. THOMPSON, D.Sc.

The author gave a *resumé* of the ordinary methods of determining the position of the plane of polarisation, pointing out their advantages and disadvantages, and exhibited his new polarimeter, in which two black glass mirrors placed at a small angle (about 2½ degrees), are used to polarise the light in two different planes. By using a modified Nicol as analyser the plane can be determined to one-tenth of a degree, when the substance examined does not absorb much light; but for dark coloured liquids, the author prefers to use one of his "twin prisms," described before the British Association in 1887 as polariser, in which the planes of polarisation are 90° apart. A method of dividing a polarised beam into two parts inclined at a variable angle, by means of a combination of quarter wave plates of mica, was described, in which the two halves of the field are similarly coloured.

Mr. GLAZEBROOK considered Poynting's glass cell with different thicknesses of active solution, a very convenient means of obtaining two beams polarised at a small angle, as by altering the strength of the solution the angle may be varied at will.

Prof. THOMPSON also read a note "*On the Formation of a Cross in Certain Crystal Structures*."

Several specimens (including benzoic acid, stalactite, Eno's salt, &c.) which exhibit a radial structure and show a cross when examined by polarised light, were thrown upon the screen, and the fact that the cross remains stationary when the specimens are rotated, demonstrated. Similar effects were produced by mica sectors arranged radially, thus showing the stationary cross to be caused by the light not being analysed in those directions.

"*On Electrical Measurement*." By Prof. W. E. AYRTON, F.R.S., and Prof. J. PERRY, F.R.S.

In a paper "On Winding Voltmeters," read before the Society in 1885, the authors showed, on the assumption that the thickness of insulating covering on wires was proportional to their diameter, that instruments wound with copper wire gave a less heating error than similar

ones wound with German silver. Since then platinoid has been introduced and the electrical constants of phosphor-bronze determined. Further, a remarkably simple relation between the volts corresponding to a given deflection on a given type of instrument, and the resistance per unit lengths of the wire used in winding it, has been suggested by Mr. Crawley. Suppose F = number of ampére turns required to produce the deflection, P and U the half area of section and volume of the coil respectively, and d and D the diameters of the bare and covered wires. Then—

$$A=\frac{F}{n_l},\quad n=\frac{P}{D^2},\quad r=\frac{4l\rho}{\pi d^2},\text{ and } l=\frac{U}{D^2};$$

rom these we get—

$$V=Ar=\frac{FU}{P}\cdot\frac{4\rho}{\pi d^2}=K\cdot\frac{4\rho}{\pi d^2}\text{ (say}$$

where K is a constant depending on the type of instrument. Since $\frac{4\rho}{\pi d^2}$ is the resistance per unit length, *the volts required to produce a given deflection are proportional to the resistance per unit length of the wire used, whatever be the material of the wire or thickness of the insulation.* Taking this into account and using a more accurate value for the thickness of the covering, it is shown that the four metals above referred to arrange themselves in the following order of merit when used for high-reading voltmeters; platinoid, phosphor-bronze, German silver, copper, and for comparatively low reading instruments, the last two change places.

As a standard ammeter of great range, a circuit containing a Depretz D'Arsonval galvanometer is shunted by a wide sheet of thin platinoid, and by altering the resistance in the galvanometer circuit the sensibility may be varied in known proportions. An instrument on this plan has been arranged to measure any current from 0·1 to 800 ampéres to ½ per cent, and the same galvanometer in series with various resistance coils is used as a standard voltmeter of practically unlimited range. Whilst arranging these standards it has been found that the deflections are not generally proportional to the currents, and the discrepancy traced to the centre of gravity of the swinging coil not being in the line of suspension. By replacing the bottom torsion wire by a long thin spring the defect may be remedied. As relating to calibration curves of intruments, it was mentioned that in "Siemens's Dynamometer," the "square law" is not correct, probably owing to distortion of the spring.

Referring to "Hot Wire Voltmeters," in which the sag of a wire heated by a current is measured by a magnifying spring, the authors remark that in their original paper on the subject they neglected the change of length due to change of stress in the wire, and subsequently their assistant, Mr. Bourne, found that maximum sensibility was never coexistent with minimum sag. The sag which gives maximum sensibility depends on the initial stress in the wire; and by altering the initial sag the instruments may be compensated for changes of temperature of the room. In the present paper the mathematical treatment is more rigorous, and the results are in accordance with experiment. A voltmeter intended for use with "electric welders," which deflects about 300 degrees for 2 volts (direct or alternating), and is graduated to 1-100th of a volt, was exhibited, and used to measure the resistance of a storage cell.

Dr. Thompson suggested that the want of proportionality of D'Arsonval's galvanometers might be due to lateral displacement of the coil caused by the current in the torsion wires crossing a magnetic field, but from experiments with pivotted coils the authors thought this improbable.

Prof. Rücker read a "*Note on the Dimension of Electro-magnetic Units*," by Prof. G. S. Fitzgerald, F.R.S., which suggests that specific inductive capacity and permeability be *assumed* to be of dimensions $[\frac{T}{L}]$ (slowness); if this be done the dimensions of quantities expressed in electrostatic and electromagnetic measure become identical. The author also states that it seems most likely that inductive capacities are related to the reciprocal of the square root of the mean energy of turbulence of the ether.

Prof. Rücker remarked that in his recent paper on the subject he considered it important to retain K and μ as secondary fundamental units, and Mr. Blakesley did not concur with Prof. Fitzgerald's suggestion.

A photograph of Crystal Models by Mr. R. T. Anderson, Belfast, was exhibited at the meeting.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, March 4, 1889.

Sir James Crichton Browne, M.D., F.R.S., Vice-President, in the Chair.

John Cope Butterfield, F.C.S., Charles Cave, Mrs. E. S. Dewick, Miss K. D. Doulton, Joseph Gordon Gordon, Mrs. Sibble Heap, Miss Mona Kemp, Lieutenant Nathaniel J. Lyon, Alfred Nobel, Richard Douglas Powell, M.D., F.R.C.P., Thomas James Reeves, B.A., F.Z.S., Mrs. W. Chandler Roberts-Austen, Mrs. H. Sutton, George Edward Whitton, M.B., Ernest H. Winstone, M.A., and Mrs. M. A. E. Wright were elected Members of the Royal Institution.

The presents received since the last meeting were laid on the table, and the thanks of the Members returned for the same.

OBITUARY.

JOHN WILLIAMS, F.C.S., F.I.C.

We much regret having to put on record the death of Mr. John Williams, F.C.S., F.I.C., which took place at his residence, 63, Warwick Gardens, S.W., on Sunday, March 3rd, within a few days of the completion of his 65th year.

The deceased gentleman was the son of John Williams, who formerly filled the position of Secretary to the Royal Astronomical Society and was connected with other learned Societies.

Mr. Williams was born in London on March 9th, 1824, and was for many years assistant to the late Mr. Morson. Subsequently he was for nearly forty years partner with Mr. King Hopkin, in the firm of Hopkin and Williams.

For seventeen years he was a member of the Council of the Pharmaceutical Society of Great Britain, during three years of which he acted as Treasurer, and for three more years he filled the office of President. Mr. Williams was at one time a contributor to the Chemical News, to which he supplied, among others, a paper on the "Preparation of Urea" (vol. xvi., p. 299), and one on the "Milligrade Graduation of Thermometers" (vol. xxxi., p. 214).

Signal Lights for Ships and Lighthouses.—A. Jaksch.—The author proposes the following mixture for distress signals:—Barium nitrate, 30 parts; magnesium powder, 20 parts; flower of sulphur, 4; and beef tallow, 7 parts. The tallow is added in a melted state, and the mixture is sifted. This mass filled into strong zinc boxes 10 c.m. in height and 8 in diameter. It gives for 20 seconds a light of 20,000 candles, visible in clear air at the distance of 100 kilometres. If the mixture is used for rockets the tallow is omitted.—*Chemiker Zeitung.*

NOTICES OF BOOKS.

Catalogue of Chemical and Physical Apparatus and Chemicals. Manufactured and Imported by Philip Harris and Co., Limited, Bull Ring, Birmingham.

The appearance of the catalogue before us is a plain proof that the need and the demand for chemical and physical apparatus and reagents is vastly greater than it was the case a quarter of a century ago. A peculiarity of Messrs. Harris's catalogue is that chemical appliances and those for the different departments of physics are not placed under separate headings, but all follow in the same alphabetical series. This arrangememt is, on the whole, convenient, since various physical apparatus are used in chemical research, and the experimentalist is thus saved the trouble of referring to separate lists for the articles which he may require. The assortment of electrical apparatus here included is very extensive. There are dynamos, batteries, accumulators, voltmeters, ammeters, friction-machines, Wimshurst's influence machines, and those of Holtz, Carré, &c. The apparatus for the production and application of heat are very numerous, including the well-known devices of Fletcher; the Hofmann, Glaser, and Erlenmeyer furnaces for organic analysis, assay furnaces, &c.

Optical instruments are not wanting; there are microscopes, polariscopes, spectroscopes, and photometers. Among chemical apparatus, properly speaking, we notice the profusion of appliances for gas analysis, both scientific and technical. We must call especial attention to the improved and very complete set for testing the illuminating power and purity of coal-gas.

Crucibles and capsules of iridio-platinum, of pure nickel, platinised nickel, copper, and silver are here mentioned.

The list of chemicals is fairly complete, and includes some rare preparations, such as yttrium oxide.

As an appendage to the catalogue, we find the lists of apparatus which the Science and Art Department require for the study of different subjects. It is curious and typically "departmental" to find diagrams showing the anatomy and physiology of the honey bee, placed not under "Animal Physiology," but under "Principles of Agriculture." For this, however, Messrs. Harris are in no wise responsible.

The illustrations are numerous and well executed, and, saving certain printing faults, the whole catalogue is admirably got up.

CORRESPONDENCE.

WARNING TO CHEMISTS.

To the Editor of the Chemical News.

Sir,—With reference to the letters which have appeared under the above heading in your issues of 13th and 20th January, and 23rd November, 1888, it may be of interest to others besides the writer to know that an individual, who has been identified under various names, is now on remand at Bow Street, and will be brought up again on Wednesday morning next.—I am, &c.,

F.I.C.

London, March 6th, 1889.

SOLUBILITY OF BRASS.

To the Editor of the Chemical News.

Sir,—I must apologise for having overlooked Mr. Blount's letter on this subject in the Chemical News (vol. lix., p. 47). He points out that my statement in the *Trans. Chem. Soc.*, 1889, p. 18, that brass dissolves in weak sulphuric acid is incorrect; and, no doubt, he is right. I used the term "brass" where I should have used "certain alloys of copper and zinc." This error does not, of course, affect the validity of my explanation of the thermal results of the action, and even if no action of the sort takes place, all that can be said is that there is nothing to explain.

My authority for the action will be found in Berthelot's *Méc. Chim.*, ii., 461.—I am, &c.,

Spencer Pickering.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 7, February 18, 1889.

On the Egyptian or Vestorian Blue.—F. Fouqué.—This very fine blue pigment, which ceased to be manufactured from the time of the fall of the Roman Empire, is a double copper-calcium silicate containing silica 63·7 per cent, lime 14·3, copper oxide 21·3, and ferric oxide 0·6. No trace of alkalies is found. It may be boiled without decomposition in sulphuric acid; ammonium hydrosulphate does not blacken it, and lime only attacks it in heat. Hydrofluoric acid is its only easy solvent. It is produced at a bright red heat, but it becomes altered if this temperature is decidedly exceeded. Vitruvius gives the following account of its preparation:—Sand and natron are ground together as fine as flour, mixed with copper filings, and the whole is made into a paste with a little water. This paste is moulded into balls which are let dry and finally heated in an earthen pot set in a furnace, so that the mass enters into fusion and turns to a blue colour. M. Fouqué finds this process successful, but there is no occasion for the sodium carbonate, potassium sulphate forming a better flux. The mass is then ground up, purified with hydrochloric acid, and finally by means of Daniell Klein's dense liquor. Magnesia cannot be used in place of lime, which is not mentioned in the formula quoted from Vitruvius. The beauty and the permanence of this pigment, which is affected neither by air, moisture, light, nor most chemical agents, the ease of its preparation, and the low price at which it can be manufactured, render it desirable that it should again come into use.

Reagents for the Mercaptan Function.—G. Denigès.—Isatin, which is already employed in a sulphuric solution to detect thiophene, is also an excellent reagent for the mercaptan function. If we mix a few c.c. of pure sulphuric acid with a small quantity of a one per cent solution of isatin in sulphuric acid and add traces of free mercaptan, or better, dissolved in a little alcohol, a fine green colour is produced, which is obtainable neither with ethyl sulphide, nor sulphurous gas, nor with hydrogen sulphide. To augment the sensitiveness of this reaction we steep the end of a glass rod, terminating in a ball in the sulphuric solution of isatin, and move it about in the atmosphere of the vessel containing mercaptan; the green colour appears very quickly even with very minute traces of mercaptan. Or, after the rod has been thus exposed for a time to the action of the mercaptan vapours its end may be plunged into a little sulphuric acid, which takes up the colouring-matter, and by repeating the operation a certain number of times the acid takes an intense colour. The presence of mercaptan may thus be detected when mixed with other volatile products without any previous separation. The green colouration is produced with the methylic, ethylic, propylic, primary butylic, isobutylic and amylic mercaptans, whilst the corresponding sulphides have no action upon the sul-

phuric solution of the reagent. The aldehyds and the higher alcohols destroy or mask the colour due to the mercaptans. In this case we may use sodium nitroprusside for their detection. The substance in question, in aqueous suspension or solution, is treated with a few drops of soda or potassa lye, shaken for a few moments, diluted with water, and the nitroprusside is added. A red-violet colour is obtained, which is not due to the production of alkaline sulphides, for no precipitate of lead sulphide is obtained on adding dilute mercaptan to an alkaline solution of lead oxide; but it is owing to the sodium or potassium derivative of the mercaptan used. If the liquid examined contains at the same time sulphuretted hydrogen or sulphides it is well to use, instead of the potassa or soda-lye, an alkaline solution of lead oxide, and then to add the nitroprusside. The black precipitate of lead sulphide thus formed does not prevent the appearance of the red colour if a mercaptan is present. The alcohol sulphides and sulphurous gas have no action upon the nitroprusside in presence of alkalies.

Preparation and Properties of Propyl and Isopropyl Fluorides.—M. Melsans.—Propyl fluoride is a gas of an ethereal odour, less pleasant than that of methyl and ethyl fluorides. It burns with a luminous flame, giving off hydrofluoric acid. At −2 under ordinary atmospheric pressure it is liquefied, forming a colourless, very movable liquid, which does not act upon glass. Its density at 20° is 2·161, theory demanding 2·175. It is very soluble in the alcohols, benzene, ether, the alcoholic iodides, and dissolves at 16° in one volume of water. The isopropyl fluoride has a more pungent odour. It burns like the propyl compound. Its density at 15° is 2·171, the theoretical value being 2·175. It is rather more soluble than the propyl fluoride, 1 vol. of water taking up 1·5 vols. of the fluoride.

On Sorbite and on its Presence in Fruits of the Family of Rosaceæ.—MM. Vincent and Delachanal.—This compound, first obtained from the fruits of the service, has since been detected in pears, apples, medlars, the fruits of the "burning bush," and in cider from Bretagne. Sorbite does not give a crystalline compound with ethylic aldehyd in presence of sulphuric acid, which distinguishes it from mannite. Contrary to what has been asserted, sorbite acts upon polarised light. It is lævo-rotatory, and its specific power is −1·73 for the ray D at the temperature of 15°.

Experimental Researches on the Degree of Affinity of Various Animal Tissues for Sulphur.—M. J. de Roy-Pailhade.—Equal weights of the different tissues of one and the same animal convert unequal quantities of sulphur into hydrogen sulphide. The descending order of tissues, established by their affinity for sulphur, is the same as the descending order established by their affinity for oxygen.

Bulletin de la Société Chimique de Paris.
Vol. li., No. 3.

Small Analytical Notes.—C. de la Harpe and F. Reverdin.

Detection of Carbon Monoxide in the Air.—The presence of this gas may be ascertained by passing the air, previously filtered, through glass-wool or cotton, over pure dry iodic acid, heated to 150°, and then into starch dissolved in distilled water. The carbon monoxide passes into the state of dioxide, a corresponding quantity of iodine is set at liberty, and the solution of starch is coloured blue. The operation is most conveniently conducted by putting the iodic acid into a small fractionation flask, the delivery tube of which has been bent down so as to plunge into a small bottle containing the solution of starch. The flask is set in an oil-bath and air is let arrive in a moderate current at the bottom of the apparatus. Other reductive bodies, such, *e.g.*, as sulphuretted hydrogen, must first be removed by known methods.

Modification of Bunsen's Apparatus for Determining Manganese and Chromates.—The apparatus is here described and figured.

On the Experiments of M. Genvresse.—Ivan Ossipoff.—The author points out the results which he obtained fifteen months ago concerning the influence of temperature on the successive chlorination of acetylacetic ether.

On a Diquinolic Base.—A. Colson.—This base has the composition $C_{22}H_{18}N_2O_3$. It is soluble in six parts of dilute hydrochloric acid and in ten parts of alcohol at 92 per cent. It melts at 71·5°. It is deposited from its ethereal solution in long flattened needles, highly double refractory, which extinguish polarised light in the direction of their length, and appear to be uniaxial and positive.

Action of Sodium upon Ethyl Cyanide. Synthesis of the Pyrrolic Derivatives.—M. Hanriot and L. Bouveault.—This memoir does not admit of useful abstraction.

On a New Ptomaine, and on a Method of Analysing Alkaloids.—A. M. Delezinier.—The apparatus is very complex, and cannot be described without the aid of the accompanying figure. The ptomaine, $C_{32}H_{31}N$, is an oily liquid, almost colourless, very sparingly soluble in water, but soluble in all proportions in alcohol, ether, toluene, and benzene. It is extremely oxidisable, and forms very deliquescent salts.

On a New Acid of Tin.—W. Spring.—The author has obtained a compound corresponding to the formula $H_2Sn_2O_7$. It belongs to the same type as disulphuric and dichromic acid, and connects tin with sulphur and its analogues. To obtain it the author takes a saturated solution of stannous chloride in water containing enough hydrochloric acid to prevent precipitation, and treats it at the ordinary temperature with an excess of pure barium peroxide. The turbid liquid thus obtained does not become clear on standing, and contains the compound of tin in the colloidal state. The barium chloride is eliminated by dialysis, and when it ceases to pass through the contents of the dialyser are evaporated on the water-bath and yield a white mass.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 4.

Conversion of Terpilene into a Menthene.—M. Bouchardat and J. Lafont.—The authors have effected this change by the prolonged action of aqueous hydriodic acid. Natural menthol ought to be attached lo the terpilene series, and it has relations of terpilenol or terpilene monohydrate, similar to those which connect the allylic and propylic alcohols.

Direct Determination of the Oxygen and Nitrogen Gases Dissolved in Natural Waters.—A. Lalien.—The author's method turns on the use of the apparatus here figured and described.

On a New Alkaloid: Imperialine.—Dr. Ch. Fragner.—The base in question is extracted from the bulbs of *Coronaria Imperialis*, and has the composition $C_{35}H_{60}NO_4$. It forms small colourless prisms, very sparingly soluble in water, sparingly soluble in ether, benzene, amylic alcohol, and petroleum ether, but very soluble in hot alcohol and chloroform. It is lævorotatory.

Alteration of the Aqueous Solutions of the Morphine Salts and their Transformation in the Organism.—Dr. Alph. Lamal (*Bulletin de l'Acad. de Belg.*).—These solutions do not alter if protected from light and from atmospheric dust. If exposed to these agents there may be formed an amorphous substance (morphetine?) and crystals of oxymorphine. Apomorphine does not

appear to be formed. Morphine circulating in the blood and the tissues is transformed into oxymorphine, which latter substance should be sought for in toxicological investigations.

Influence of Diet upon the Melting-point and the Chemical Composition of Butter.—Ad. Mayer (*Landw. Versuch. Station*).—The volatile fatty acids rise and fall with the density of the butter fat. The melting-point of butter-fat is not in relation either with the density or the proportion of the volatile fatty acids, and depends upon the quantity of oleine rather than upon that of butyrine, caproine, &c. The total of the volatile fatty acids, and consequently its density, varies even for one and the same cow within much wider limits than it has been hitherto thought. It depends on the period of lactation, and falls as it is more advanced. Beet-root, grass, and green clover are most favourable; then follows hay, and lastly ensilage.

Detection of Alcohol in Essential Oils.—H. Hager (*Pharm. Zeitung*).—The author agitates the sample in question with glycerin, which removes the alcohol totally.

Adulteration of Vanilline.—Em. B. (*Gehe's Handelsbericht*).—The presence of benzoic acid may be detected by means of the microscope, as vanilline crystallises in needles and benzoic acid in minute laminæ.

Presence of Tyrotoxine in Ices and in Poisonous Milk.— Dr. C. Vaughan (*Archiv. f. Hyg.*).— The substance of this paper has been already noticed.

A New Reagent for Glucose.—L. Crismes (*Pharm. Zeitung*).—This reagent is safranine, the solutions of which are reduced and rendered colourless by glucose.

Revue Universelle des Mines et de la Metallurgie.
September, 1888.

Volumetric Method of Determining Manganese.—A. Ghilian.—The hydrochloric solution of the substance containing the manganese in the manganous state diluted with boiling water is poured into an Erlenmeyer flask holding from 900 to 1000 c.c. and mixed with an excess of zinc oxide suspended in water. The liquid is made up to 500 to 600 c.c. by means of boiling water and the standard solution of permanganate is slowly dropped in from a Mohr's burette, agitating after each division, and causing the oxides to settle by slanting the flask. The colour of the clear supernatant liquid shows the precise moment when it is coloured by an excess of permanganate. From the volume of permanganate employed the proportion of manganese is calculated. In the treatment of irons, steels, Bessemer metal, and ores whose proportion of manganese does not exceed 3 to 4 per cent the author uses a solution containing 4 grms. permanganate per litre, the value of which is 0·000213 per $\frac{1}{10}$ c.c. (*i.e.*, for one division of the burette). A solution of double the strength is employed for the determination of spiegels, ferro-manganeses, and rich ores. Its value is 0·000426. Twenty-five such assays may be executed in half-an-hour. The zinc oxide employed ought to be the kind obtained by precipitation. During the operation the liquids should be kept at about 80°.

October, 1888.

Studies on the Raw Materials and the Products of Siderurgy.—Dr. C. Meinecke (*Zeitschrift fur angewandte Chemie*).—The first chapter of this series treats of the precipitation of manganese as sulphide. The author finds that this process is free from inconvenience if we obtain the green anhydrous manganous sulphide, which is granular in texture, deposits rapidly, and can be collected on a filter and quickly washed with a small quantity of water; it shows no tendency to give a turbid filtrate. To obtain the sulphide in this condition the author proceeds as follows:—The boiling manganous solution is treated with a large excess of ammonia, and without stopping the ebullition or attending to the precipitate, if one is formed, a decided excess of ammonium sulphide is added. The ebullition is still kept up for a few minutes, and the liquid is then let settle and filtered when it has become clear. Traces of the green sulphide which remain in the filtrate may be recovered by expelling the ammonia by evaporation, decomposing the residual ammonium sulphide by a little hydrochloric acid, filtering off the deposit of sulphur, concentrating the filtrate, and precipitating the manganese with bromine and ammonia.

Removal of Fused Masses from Platinum Crucibles.—Professor L. L. de Koninck.—This process is devised for the extraction of fused masses obtained in consequence of disaggregations by alkaline carbonates, sulphates, &c. When the fusion is complete the author immerses vertically in the centre of the melted mass, the spiral extremity of a strong platinum wire, 0·5 m.m. in thickness and 8 to 10 c.m. in length, with a loop at its upper end. The wire is kept in this position until the mass solidifies. When completely cold the crucible is suspended by means of a second platinum wire, hooked to the former and attached to a glass hook supported a few millimetres above a triangle of platinum or of pipe-stems. The crucible is then rapidly heated by means of a strong lamp, and as soon as the outside layer of matter in contact with the matter enters into fusion, the crucible falls down upon the triangle and the mass which remains solid is suspended on the wire. This wire is immediately seized with the forceps with one hand and lifted away from the crucible, whilst with the other hand the lamp is removed.

MISCELLANEOUS.

Examination of Alcohol.—H. Bornträger.—A specimen of the alcohol is diluted with much water, observing if oily drops collect on the surface. If this is the case the spirit is tested for acetal with sulphuric acid and potash-lye (odour of acroleine) and for amylic alcohol with strong hydrochloric acid and aniline oil. A second sample is tested for aldehyd with potassium iodide and a solution of acid sodium-magenta sulphite. If no drops appear on the surface, test as above for aldehyd, dilute a further portion with two parts of water, shake up with chloroform, separate, let evaporate at a gentle heat, and test any residue for acetal and amylic alcohol as above. —*Zeitsch. f. Anal. Chemie*, Vol. xxviii., Part 1.

Coloured Reactions of Strychnine.— Flückiger (*Pharm. Zeitung*) refers the colours which strychnine produces with sulphuric acid and oxidising agents (lead peroxide, potassium chromate, ammonium vanadiate, ceri-cerous oxide, potassium ferricyanide, and permanganates) to the formation of one and the same lilac or violet product, which is very unstable. A permanent and certain colour is obtained with the following solution:—0·01 grm. potassium dichromate is dissolved in 5 c.c. of water and mixed with 15 grms. (8 15 c.c.) sulphuric acid of sp. gr. 1·84 at 15°. When cold the reagent is ready for use. A solid body to be tested for strychnine is moistened with a single drop of this liquid, or the powdered solid is scattered upon the liquid on a porcelain slab, or a saturated solution of the strychnine salt is let flow slowly over the acid, shaking very gently so as to obtain a distinct zone. Certain substances, such as brucine, give a fine red colour with the chromiferous sulphuric acid, and mask the reaction of strychnine. In case of a mixture of brucine and strychnine which does not at once give the strychnine reaction, the substance is placed upon a small moistened filter and chlorine-water is dropped upon it as long as a red colour is thus produced. Dichlorbrucine is thus formed as an amorphous, easily soluble body, which passes rapidly into solution. The undissolved alkaloidal residue gives the reaction of pure strychnine.

Reactions of Alkaloids.—Fr. Kundrát recommends as a reagent a solution of ammonium vanadiate in strong sulphuric acid, 0·1 grm. in 10 c.c. acid. It is applied in the same manner as Frœhde's mixture. It gives with aconitine a light coffee-brown; with atropine, a red, passing into yellowish red and finally into yellow; apomorphine, a dark violet blue, then dirty green, and by degrees red-brown to light brown; brucine, intense blood-red, gradually fading to the original colour; cinchonine, an insignificant orange, slowly turning greenish; cocaine, orange; codeine, greenish brown, gradually darkening, finally brown; colchicine, green, then brownish green, and finally coffee-colour; coniine, intense green, gradually becoming browner; digitaline, intense dark brown with a reddish cast, finally a quite dark brown; quinidine, an unimportant bluish green; quinine, faint orange, then bluish green, and lastly greenish brown; caffeine, no reaction; morphine, brown, like digitaline; narceine, brown, passing into dirty blue violet with a brownish cast, then gradually becoming reddish brown; narcotine, intense blood-red with a carmine cast; nicotine, slightly darker, the original colour soon returning; papaverine, violet with a brownish cast (similar to the veratrine reaction) becoming gradually bluish green, and lastly orange yellow; picrotoxine, slightly darker, fragments of the dry substance are coloured an intense orange; pilocarpine, light orange; piperine, intense red-brown to black-brown, fragments of the dry base touched with the reagent turn black; physostigmine, greenish yellow, then crimson, lastly yellowish brown; salicylic acid, brownish green, gradually darkening; antifebrine, crimson, then brown; antipyrine, intense green-blue, turning more to a blue; kairine, dirty rose colour, then dirty light brown, and finally dirty greenish brown; santonine, no action; solanine, coffee brown, the drop becoming crimson at the edge, yellow within and dirty green at the centre; after about two hours the drop becomes a dark blue gelatinous mass; strychnine, violet blue, turning to red violet, carmine red, and lastly a splendid a fire red. If dry strychnine is touched with the reagent it takes a fine violet blue; veratrine, red-brown, then dark violet red.—*Chemiker Zeitung.*

MEETINGS FOR THE WEEK

MONDAY, 11th.—Medical 8.30.
—— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.

TUESDAY, 12th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Royal Medical and Chirurgical, 8.30.
—— Sanitary Institute, 8. "Water Supply, Drinking Water, Pollution of Water," by Dr. Louis Parkes.

WEDNESDAY, 13th.—Society of Arts, 8. "Aluminium and its Manufacture by the Deville-Castner Process," by William Anderson, M.Inst.C.E.
—— Pharmaceutical, 8.
—— Microscopical, 8.

THURSDAY, 14th.—Royal, 4.30.
—— Royal Institution, 3. "The Venom of Serpents and Allied Poisons," by Sidney Martin, M.D.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.

FRIDAY, 15th.—Royal Institution, 9. "Beacon Lights and Fog Signals," by Sir James N. Douglass, F.R.S.
—— Sanitary Institute, 8. "Ventilation, Measurement of Cubic Space, &c.," by Sir Douglas Galton, F.R.S.

SATURDAY, 16th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that Professor CURT NETTO, of 16, Lindenaustrasse, Dresden, Germany, has applied for leave to amend the Specification of Letters Patent No. 4228 of 1887 for "Improvements relating to the extraction of Aluminium from substances containing the same."
Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 27th February, 1889.
Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)
H. READER LACK,
Comptroller-General.

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THE CHEMICAL NEWS.

VOL. LIX. No. 1529.

ON THE TRUE FORMULA FOR PERMANGANATES.*

By CHARLES M. BRADBURY, of Virginia.

(Continued from p. 117).

THE periodic system of the elements has been brought to a stage of development which places it, at least as to its main facts, in the realm of accepted truth; and it may be appealed to for the decision of many doubtful questions with great confidence in the answers given by it. Now the atomic weight of manganese is well established; and according to the Periodic Law, *i.e.*, that the chemical properties of the elements are a periodic function of their atomic weights, manganese is forced, by virtue of its atomic weight, into the group of *heptad elements*, at the same time preserving its close relationship with the metals of the iron group. This may be seen by reference to a scheme or table of the periodic system. Even this bare fact would be conclusive, unless manganese could be shown to be an exception to the periodic law. Moreover, the relationship of manganese to the halogens may be received as not by any means incredible; for the behaviour of the elements in general, when viewed in the light of this system, indicates that under the influence of varying valence elements which are commonly far from alike may develop strong similarity. We may take, as examples of this variation in character of the same element, the marked differences between the *ous* and the *ic* compounds of iron, chromium, copper, and other metals, and between the acid and basic oxides; and the evident tendency of the metals in their higher oxides to assume functions identical with those of acidic elements.

An obvious objection to the verdict of the periodic system is that it seems to leave no room for the perfectly well-established dyad, tetrad, and hexad valence of manganese in many of its compounds, but declares it simply heptad. As to this, similar objections hold with many elements. The answer for all is found either in Prof. Muir's definition of valence:* "The valency of an elementary atom is a number which tells the *maximum number* of monovalent atoms (*i.e.*, atoms of H, F, Cl, Br, I, or Tl), with which the given element combines to form a molecule," or, perhaps better, in the distinction made by Prof. Richter† between hydrogen valence and halogen or oxygen valence; or, finally, what amounts to the same thing, in the difference between true valence and the "index of affinity,"‡ deduced from consideration of the highest oxides. The first of these explanations is simple and, I believe, applicable in every case, but it seems likely that the others must also be reckoned with in interpreting the indications of the periodic system. However this may be, it is clear that we may either limit the meaning of "valence," as Muir does, in which case no room remains for any law whatever about variable valences, or we may use Richter's or Meyer's distinction between "hydrogen" or "real valence," subject to the law of variation by twos only, and "oxygen or halogen valence," or "index of affinity." In either case the impossibility of supposing that manganese can display an odd number of atomicities can no longer be alleged.

If, then, we assume that the valence of the manganese in permanganates is identical with that displayed in the highest oxide, Mn_2O_7 (this being, like that of the halogens in their highest oxides, heptad§), the chief objections to the formula $\overset{I}{R}MnO_4$—that it violates the law of even numbers, and that it does not correspond to any structural formula—disappear at once. If we represent manganese heptoxide as—

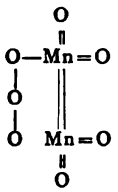
* Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $\overset{n}{R}(MnO_4)n$.

* "Principles of Chemistry," 122.
† "Inorganic Chemistry," 164.
‡ Lothar Meyer. See R. and S., II., ii., 511.
§ R. and S., II., ii., 512.

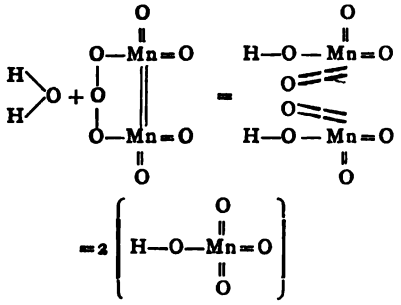
THE PERIODIC SYSTEM.

The following table is from Richter's "Inorganic Chemistry," except that the atomic weight of titanium (48) has been supplied from Roscoe and Schorlemmer's "Treatise."

		I. Group.	II. Group.	III. Group.	IV. Group.	V. Group.	VI. Group.	VII. Group.	VIII. Group.		
H Compounds.		—	—	—	MH_4	MH_3	MH_2	MH			M_2H
Highest salt-forming oxides.		M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3	MO_2	MO
Periods.	Series.	H 1									
1st	1st	Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
2nd	2nd	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35			
3rd	3rd	K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 58	Ni 58
	4th	Cu 63	Zn 65	Ga 70	— 73	As 75	Se 79	Br 80			
4th	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 104	Rh 104	Pd 106
	6th	Ag 108	Cd 112	In 113	Sn 118	Sb 122	Te 126	I 127			
5th	7th	Cs 132	Ba 137	La 139	Ce 140, Di 144	—	—	—	—	—	—
	8th	—	—	—	—	—	—	—			
	9th	—	—	Yb 173	—	Ta 182	W 184	—	Os 193	Ir 193	Pt 196
	10th	Au 197	Hg 200	Tl 204	Pb 206	Bi 210	—	—			
		—	—	—	Th 234	—	M 240	—			



(which suggests that loose union, which really exists, of a portion of the oxygen), then, upon contact with water,



or $H_2O+Mn_2O_7=2HMnO_4$, and similarly for K_2O, Na_2O, &c.

(To be continued).

MAGNETIC VISCOSITY.

By THOMAS T. P. BRUCE WARREN.

WHEN experimenting on the magnetic permeability of oils and other liquids I found that if a magnetic substance, like soft iron, be covered by different liquids not only was its susceptibility modified by the permeability of the intervening medium, but distinct evidence was obtained in every case of a molecular stress being produced in the medium, and which indicated itself by a decided tendency of a balanced magnet to stick, as it were, when it was allowed to remain a short time over the soft iron.

The explanation seems to be that the maximum effect of a magnet on soft iron depends on the rapidity with which the medium accommodates itself to the constrained condition necessary for the soft iron to take its greatest degree of magnetisation.

As time is an element of importance in attaining a full maximum magnetisation from any magnet of a certain intensity, it is not unreasonable to suppose that when a *non*-magnetic medium has been so constrained by the lines of force passing through it that the molecular stress, which is also favourable to an increased magnetisation of the soft iron, will retain the magnet with a slight but decided extra force. I propose to call this extra force, which is due to molecular stress, *viscosity*.

Viscosity is more probably a function of permeability. We have the magnet acting across the medium to the soft iron, and conversely, the soft iron reacting through the same medium to the magnet, until the molecular arrangement of the medium accommodates itself to a maximum.

If a galvanometer needle, suspended in the usual way, be forcibly deflected by a current, it is found that the needle regains its fiducial position very slowly; this has been attributed to a crushing effect on the fibres. This effect has been called viscosity. I do not think it is entirely due to mechanical causes. The term as used in this communication is applied to a very similar phenomenon.

The experimental arrangement was as follows:—A balanced horseshoe magnet was suspended from one of the arms of a balance. Immediately under the magnet was placed a shallow specimen glass (salvers) with the usual flat glass cover. The cover prevented the magnet being wetted with the liquid, and allowed the attraction to be balanced through a uniform depth of liquid. The soft iron rested on the bottom of the glass.

When the magnet was allowed to rest on the cover for a short time, it required an increased weight being placed in the other pan to pull the magnet off, than when the magnet was momentarily in the same position, or only for so long as to restore equilibrium in the balance.

I propose giving some experimental results on a future occasion, and to point out its importance as an adjunct to analytical research.

PHOTOGRAPHIC MAP OF THE NORMAL SOLAR SPECTRUM.

(SECOND SERIES).

Made by Professor H. A. ROWLAND.

A NEW and greatly improved edition of this map, extending from the extreme ultra violet down to and including B to wave length 6950, is now ready. The old map, published in 1886, was made by means of a grating ruled on the old dividing engine, which was originally intended for only small gratings, and at a time when Professor Rowland's knowledge of photography was limited. Furthermore, it was not printed in a sufficiently careful manner, and the negatives, which were originally none too good, soon became broken or defaced, so that many of the prints, especially the later ones, were not satisfactory.

The whole work has now been gone over again. A new dividing engine to rule large gratings has been constructed and has proved to be superior in every way to the old one, although the old one is almost equal to it for small size gratings. It has been placed in the vault of the new physical laboratory, where an almost constant temperature is maintained. Several concave gratings of 6 inches diameter and 21½ feet radius have been ruled with 10,000 or 20,000 lines to the inch, giving definition hitherto undreamed of. These have been mounted in the best possible manner. The laboratory contains rooms for developing, making emulsions and dry plates, complete enlarging apparatus, and, indeed, every facility for photographic work on the spectrum of the sun, and a large steam engine, a variety of dynamos, continuous and alternating current, with Ruhmkorff coils of all kinds, one of which latter will melt down iron wire larger than $\frac{1}{16}$ inch diameter in the secondary circuit, give means of future investigation on the spectrum of the elements. Professor Rowland has devoted years to the making of dry plates, simple and orthochromatic, and is thus better prepared than before for the work of making the map. He has also revised his list of standard wave lengths and extended them into the ultra violet, and has placed the scale upon the photographs with greater care than before. The printing is carried on in Baltimore, where it is under the immediate supervision of Professor Rowland.

The negatives have been made on thick French plate-glass and the prints are much more artistic than the old ones. The definition is not only much finer throughout, but the prints are much more uniform and have fewer spots.

The process of making this map is the same as that used for the old one, and is based on the property of the concave grating as discovered by Professor Rowland: this property is that the spectrum, as photographed in any given order, is normal and of the same scale throughout. The focus remains automatically adjusted, so that one has only to move the instrument to the part of the spectrum required, absorb the overlying spectra, and put in the photographic plate. The negatives enlarged have been

selected from many hundreds taken from different gratings, though three gratings were finally selected for the work. The negatives from any given order of spectrum are measured from one standard line to another on a dividing engine, so that the constant of the dividing engine is known. The scale is then made by ruling on a piece of French plate-glass having a coating of blackened collodio-chloride. The negatives are then clamped to the scale firmly, after being adjusted into position by the standards. They are then put in the enlarging apparatus and the whole enlarged from 2½ to possibly 4 times, so as to make the scale of the map about three times that of Angström's map. The positives thus made are then figured, and negatives made from them by contact.

In the negatives so far examined the scale has been placed within less than $\frac{1}{10}$ Angström division or $\frac{1}{100000}$ wave length of its true position.

As to the definition, much is lost in the enlargement, not so much from want of definition in the enlarging lens, a 25 × 21 inch Dallmeyer rapid rectilinear, as from the radical defect of phogographic processes: for when one brings out the fine doubles in which the streak of light in the centre is very faint, he loses many of the fainter lines. The original negatives show E, and even finer lines like that at wave lengths 5276·1 and 5914·3 plainly double, but there is little hope of showing this on the map.

The atmospheric line just outside of one of the D lines also nearly merges into it, although in the original negative it is widely sundered from it.

However, there are few instruments which will show more of the spectrum than can be found on the map, even below the D line where cyanine and chlorophyll plates had to be used, for the first line in B is shown widely triple. Above, and including the D line, the definition rapidly improves, and a low power magnifier must be used to bring out the full definition. However, from wave lengths 5300 to 3800 the superiority over the old edition is not so marked as above and below this. In the ultra violet above H there is an immense improvement in the new, both in definition and in the quality of the photograph.

As to comparison with other maps of the spectrum made by measurement and drawing, it may be said that no comparison is possible. The photograph is the work of the sunlight itself and the user of this map has the solar spectrum itself, before him, and not a distorted drawing full of errors of wave length and of intensity. The superiority is so great that there is no possibility for comparison.

The following is a list of the plates, each 3 × 2 feet, containing two strips of the spectrum.

a	includes	from	wave length	?	to 3350
b	,,	,,	,,	3270	,, 3730
c	,,	,,	,,	3670	,, 4130
d	,,	,,	,,	4050	,, 4550
e	,,	,,	,,	4450	,, 4950
f	,,	,,	,,	4850	,, 5350
g	,,	,,	,,	5250	,, 5750
h	,,	,,	,,	5650	,, 6150
i	,,	,,	,,	6050	,, 6550
	,,	,,	,,	6450	,, 6950

Negatives b, c, d, e, f, g, h, i, j, are now ready, although that for i is too irregular to be entirely satisfactory and it may be replaced. The plate a to the extremity of the solar spectrum will be attempted this summer, but may cause much trouble and delay, and will be sold as an extra plate. The prints are on heavy albumen paper mounted on cloth.

The cost of printing has been so much increased that the prices for this new series will be greater than for the old one, but scarcely more than covers the cost of the printing.

The plates will be delivered in Baltimore or New York or will be sent by express or mail, securely packed, at the charge and risk of the purchaser, at the following net prices:—

Set of nine plates, wave length 3270 to 6950, 18 00 dols.
Single plates, ... 2 50 ,,

Should any extra plates continuing the spectrum in either direction be published, subscribers can have them at 2.00 dols. each.

Subscribers to the old edition will have the preference in the delivery of the new one and a reduction of 10 per cent in the price. The three plates h, i, j, to complete their set, will be furnished for 6.00 dols. They are advised to take g also, as the old map of that region was bad. The four, g, h, i, j, will be furnished to them for 8.00 dols.

Extra Plates.

Two plates, each 3 × 2 feet, suitable for framing and hanging on the wall, have been made of the B and D lines. The latter are 3 inches apart, and the former has an extent of about 24 inches. Enlargements of some of the carbon bands from the arc electric light have also been made. They show the wonderful structure of these bands, each containing many hundred lines, each one of which is a close double or, in some cases, a triple. These plates will be sold for 2.25 dols. unmounted, or 2.50 dols. mounted on cloth.

No plate will be given away or sent in exchange.

Remittances may be made by draft or money order. All subscriptions and orders should be sent and remittances made to the

Publication Agency of the Johns Hopkins University,
Baltimore, Md., February, 1889.

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

WITH AN ACCOUNT OF THE METHODS OF ANALYSIS EMPLOYED.*

(Continued from p. 115).

By FRANK AUSTIN GOOCH
and JAMES EDWARD WHITFIELD.

Carbonic Acid.—The greater number of the waters with which we have had to deal were hot when the sample was taken, and not surcharged with carbonic acid. In view of the circumstances under which the waters were collected it was thought that a portion of the general sample, which was carefully sealed, might be made to serve the purpose of determining the carbonic acid contained in the water, instead of portions taken specially for that end and treated in the field with a mixture of ammonia and calcium chloride to fix the carbonic acid gas. Accordingly, dependence was placed upon the large general sample for this estimation. The presence of free silica in the waters, and the complexity of composition, place so great an obstacle in the way of determining the *free carbonic acid* that the attempt to make the estimation was not undertaken. The method which we adopted for the determination of the *total carbonic acid* is that well-known process which rests upon the boiling of the acidified liquid, and the absorption and weighing of the gas evolved. The apparatus which we employed, differing somewhat from that in ordinary use for this purpose, is shown in Fig. 1. It consisted eseentially of a flask in which to boil the water, a cooler to return the condensed steam to the flask, a U-tube filled with anhydrous cupric sulphate to intercept traces of hydrochloric acid, which might escape condensation in the cooler, a second U-tube charged with calcium chloride to dry the gas, potash bulbs to retain the carbonic acid, and two tubes filled with calcium chloride, one of which was to retain the moisture carried over from the potash bulbs and was weighed with them, the other serving to protect the weighed tube from the action of the external

* *Bulletin o the United States Geological Survey*, No. 47.

air. Through the rubber stopper of the flask passed the tube of a separating funnel, the end of a condensing tube, and a tube which connected the interior of the flask with the system of bottles and scrubbing tower, which furnished at will and under slight pressure a supply of dry air free from carbonic acid.

Before beginning the operation of determining the carbonic acid in a water, the atmospheric air was expelled from the apparatus and replaced by pure air free from carbonic acid. The stop-cock in the funnel tube and the connection with the aspirator having been closed, the water started through the cooler, and the joint broken between the potash bulbs and the drying tube immediately preceding it, a few c.c. of distilled water were put into the flask and boiled. The steam generated drove the air from the flask, and that remaining in the tubes was swept forward by pure air admitted from the aspirator. The outer opening of the tube at the end of the line was closed, the source of heat removed, and the flask allowed to fill with air from the aspirator. The whole apparatus having been filled thus with air free from carbonic acid, the water to be examined—we found 200 g. to be a convenient amount—was introduced into the flask through the funnel tube and followed by a little boiled water and a sufficiency of sulphuric acid, care being taken to exclude the outer air during the operation. The connection between the line of drying tubes and the absorption bulbs was re-established, the liquid in the flask was brought to the boiling-point, and to secure constant and quiet ebullition as well as to aid in transferring the carbonic acid from the flask to the absorption bulbs, a current of pure air was sent slowly through the boiling liquid, which covered the end of the aspirating tube and that of the funnel tube. At the end of half an hour the burner was removed from under the flask and the apparatus was permitted to cool during another half hour, the current of air being kept in motion through it. The difference between the weights of the potash bulbs, with the drying tube which accompanies them, before and after the operation, was taken to be the weight of carbonic acid absorbed, and the *total carbonic acid* of the portion of water examined.

When the water under examination contained hydrogen sulphide, a little cupric sulphate was introduced before acidifying into the portion which was serve for the determination of carbonic acid.

Arsenious Acid and Boric Acid.—To the portion taken for analysis—usually 500 g.—hydrochloric acid was added in distinct excess, the temperature of the liquid was raised to 70° C., and the source of heat having been removed, hydrogen sulphide gas was introduced in a gentle current for several hours. The precipitation of the arsenious sulphide began at once, but the action of the precipitant was continued to insure completeness. The precipitate was collected upon an asbestos felt, washed, and dissolved in fuming nitric acid. The solution in nitric acid was evaporated to dryness, the residue was dissolved in hydrochloric acid, and from this solution, made strongly ammoniacal, but kept small in volume, the arsenic was precipitated by the addition of the magnesium chloride mixture and brisk agitation. The precipitated ammonium-magnesium arsenate was allowed twelve hours in which to settle, and was then transferred by means of the mother liquor without the use of other liquid to a perforated crucible carrying an asbestos felt, washed thoroughly with the mixture of one part of ammonia to three of water, usually employed for this purpose, but with the sparing use of the washing material which this mode of filtration permits, dried carefully, ignited gently at first, and at a low red heat afterwards, in an atmosphere of oxygen

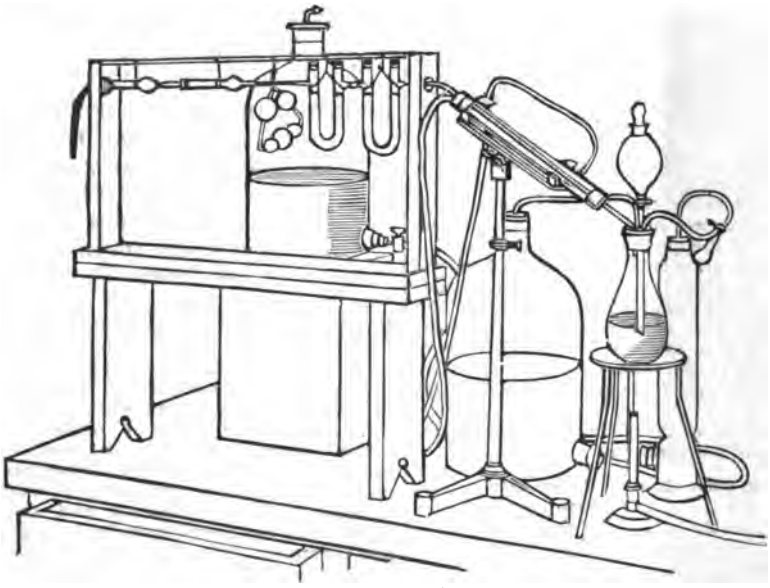


Fig. 1.—Apparatus for the Estimation of Carbonic Acid.

The great faults of this process, originally Levol's, have been the solubility of the precipitate in the mother liquor, and more especially in the ammoniacal wash water, and the difficulty in drying or igniting the precipitate collected on paper. These sources of inaccuracy vanish, however, so completely with the use of the asbestos filter, and due care in keeping the volume of mother liquor and the washings small, that the filtrate, freed from ammonia, acidified and charged with hydrogen sulphide, fails to yield arsenious sulphide. As a test for the presence of arsenic, the method has enjoyed an excellent reputation, and in the form in which we have made use of it we believe it to be exact.

The filtrate from the precipitate of arsenious sulphide, containing all the boric acid, was nearly freed from hydrogen sulphide by the transmission of air, and the chlorine, with residual traces of hydrogen sulphide, was removed by treatment with silver nitrate and filtration.

The filtrate from the precipitated sulphide and chloride was treated with sodium hydrate in quantity, a little more than sufficient to precipitate the excess of silver as completely as may be. The whole was evaporated until the precipitate took on a compact and granular form, then filtered, and the filtrate was evaporated nearly to dryness. The residue was treated with nitric acid, first just to acidify, and then with a sufficient (measured) amount to make it certain that the boric acid was entirely free. The concentrated solution of the nitrates, nitric acid, and boric acid was drenched with methyl alcohol to precipitate the first and dissolve the last. The solution of boric acid was quickly separated from the precipitate by means of the vacuum filter, and the residue washed sufficiently with methyl alcohol. When much boric acid is present the precipitated nitrates should be dissolved in water, and the process of precipitation with methyl alcohol repeated; but when small quantities are dealt with, as was the case in the most of our work upon these waters, a single treatment leaves no boric acid in the residue. From the solution in methyl alcohol, the boric acid was separated and its amount estimated by a method devised by one of us and described elsewhere in full.*

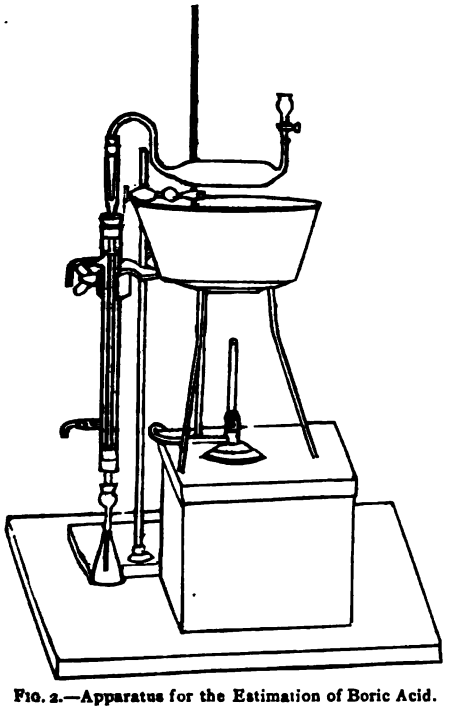


Fig. 2.—Apparatus for the Estimation of Boric Acid.

This process consists essentially in distilling to dryness the solution in methyl alcohol, containing free nitric acid and nitrates, and treating the residue by successive drenchings with methyl alcohol and distillations. The distillate, carefully protected, contains at the end of the operation all the boric acid, and this is fixed as calcium borate by the evaporation of the distillate over lime. The difference between the weight of ignited lime and the weight of the same after having been submitted to the action of the alcoholic solution and ignition, is the weight of boric anhydride in the solution.

The distillation was effected by means of an apparatus which consists of retort, condenser, and bath for heating (Fig. 2). For the last a bath of paraffin is on the whole most convenient. The condenser is set vertically to facilitate changing the level of the retort within the bath, and to secure at the same time continued and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel tube provided with a stop-cock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus; but it is convenient to attach, to receive the distillate, a small Erlenmeyer flask, which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out the distillation the liquid is introduced into the retort either by the funnel tube or previous to its insertion, the glass stop-cock is closed, the water started through the condenser, and the retort lowered into the hot paraffin, care being taken to begin the operation with the retort not more than half full, and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty and requires little care. The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a pipette of 200 c.m.^{3} capacity makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 c.m.^{3} of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0·7 c.m. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid to be distilled boils—something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol—and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet and without actual boiling.

Experiment showed that six successive treatments by drenching with 10 c.m.^{3} of methyl alcohol and distillation to dryness were more than adequate to remove 0·2 grm. of boric anhydride entirely from a residue containing 2 grms. of sodium nitrate; but, in order to break up the crusted residue, which by its insolubility in the alcohol might effect to some extent the protection of the boric acid from the action of the alcohol, it was found best to introduce and evaporate 2 c.m.^{3} of water between the second and third, and again between the fourth and fifth distillations. In most of the cases with which we were concerned in the work upon these waters, four treatments by drenching and distilling, with one intermediate moistening with water, were entirely sufficient to volatilise the boric acid; but in every case the residue was examined for boric acid by the exceedingly delicate turmeric test, taking care to first oxidise nitrites by means of bromine, and to expel the last before applying the test.

When the solution of boric acid in methyl alcohol is put over lime and evaporated at once some volatilisation of the boric acid is apt to take place; but a short period of digestion—from five to fifteen minutes—is sufficient to fix the boric acid completely.

To secure the proper exposure before evaporation, with the least delay, the lime which is to retain the boric acid, first ignited in the crucible in which the evaporation is to be made subsequently, is transferred to the receiving flask attached to the condenser before the distillation is begun, and so has opportunity to exert its action upon the boric acid as the distillation progresses. At the end

* *Bulletin of the United States Geological Survey*, No. 42. *Am Chem. Journ.*, vol. ix., p. 23.

of the distillation the distillate containing the alcohol, boric acid, nitric acid, and lime, is transferred again to the crucible, evaporated to dryness at a very gentle heat, and ignited to a constant weight over the blast-lamp. The greatest care is to be taken to secure similarity of conditions under which the crucible and lime are weighed before and after ignition, and definite periods of cooling before weighing—ten minutes is a suitable time—should be allowed to pass, in order to eliminate, as far as possible, the effect of atmospheric condensation upon the large surface of platinum.

The tendency of the process is to yield figures slightly larger than the truth, as was shown in the test analyses which are given in the full description of the process, to which reference has been made. In distilling 0·2 grm. of boric anhydride and fixing it in 1·5 grms. of calcium oxide, the mean error was shown to be about 0·0010+grm. In the work upon the waters parallel determinations rarely differed by more than that amount.

Chlorine (with Bromine and Iodine).—The precipitation of chlorine, together with bromine and iodine, was usually effected without difficulty by treating the weighed portion of water—from 100 g. to 500 g., according to the circumstances—with nitric acid to a slightly acid reaction and silver nitrate in excess, directly and in the usual manner, excepting that the operation was effected in the cold, and that the whole was allowed to stand quietly in the dark for several hours to secure perfect subsidence of the precipitate. In only one or two cases did the silica, which the waters carry abundantly, give rise to trouble in the precipitation. In such cases comparative tests were made as just described upon portions treated previously with an excess of pure sodium hydrate, it having been noticed that certain very siliceous waters, which of themselves very quickly filled the pores of the filter with an invisible coating of silica, could be made to filter with rapidity by first treating them with sodium hydrate in excess, and then with nitric acid to slight acidity. Treatment with acid alone did not bring about the desired condition of the silica. In the case of the water of the Coral Spring the proportion of silica is so great and its character such that to secure satisfactory results we were obliged to convert the silica to hydrofluosilicic acid by the addition of hydrofluoric acid and nitric acid before precipitating the silver salt. The silver chloride (including the bromide and iodide) was collected upon asbestos in a perforated crucible, dried directly over the free flame of a Bunsen burner turned very low and at a temperature below its melting-point, and weighed. In the case of waters containing hydrogen sulphide in quantity precipitable by silver nitrate, the portion for analysis was rendered ammoniacal before the addition of the silver salt, and the precipitated silver sulphide was filtered off. The silver salts of the halogens were then precipitated from the filtrate by nitric acid, and the process was completed as described.

(To be continued).

THE ANALYSIS OF SUBSTANCES CONTAINING ALUMINA, LIME, AND MAGNESIA.

By L. BLUM.

The author some time ago pointed out the differences which may occur in the precipitation by ammonia of a mixture containing alumina, ferric oxide, and phosphoric acid. To avoid these irregularities he recommended to effect the precipitation with a slight excess of ammonia, and not to expel it by prolonged boiling, since it is not easy to hit the exact moment when all superfluous ammonia is expelled without an incipient splitting up of the ammonium chloride present into ammonia and hydrochloric acid. This opinion ran counter to the well-known fact that lime and magnesia can be perfectly separated from alumina and ferric oxide only by prolonged ebullition in presence of ammonium chloride. In accurate analyses R. Fresenius even recommends a repeated precipitation to effect complete separation. The author also has always found small quantities of lime in precipitates which had been re-dissolved. He therefore sought to determine the effect of the method of precipitation which he recommends upon the separation of the lime and the magnesia. He therefore instituted two series of experiments, in one of which (A) are given the results of a single precipitation with ammonia, and in the other (B) the results of a twofold precipitation. The proportion of alumina and ferric oxide in B was smaller than in A, as it was to be expected, but the lime also decreased simultaneously. In the precipitate obtained by the twice repeated action of ammonia, lime and magnesia were entirely absent. The lime carried down by ammonia in the first precipitation is in the mean 0·26 per cent. But this difference is small in comparison with that which may be produced by a prolonged boiling of the precipitated solution. If the excess of ammonia added is considerable, a repeated precipitation involved a total loss of 0·39 per cent. Special experiments proved that the decrease of lime could not be due to a solubility of calcium oxalate in water containing ammonium chloride. The chief part of the mean loss of 0·39 per cent comes upon the magnesia, though the results in Series B are rather higher than in Series A. When the precipitation of the alumina is repeated it is absolutely necessary, as Fresenius recommends, to evaporate the filtrate from the calcium oxalate to dryness and ignite the residue in order to expel the ammoniacal salts.

C. Meinecke, in a paper in the *Zeitschrift fur Angewandte Chemie*, has since found that in a single precipitation with ammonia and without boiling a complete separation of alumina and ferric oxide from lime and magnesia is not practicable. He finds that without such boiling his precipitate contained 0·72 per cent of lime and magnesia. The author, on the contrary, finds a difference in the alumina of 2·99 per cent. This he considers a proof of the correctness of his assumption that on prolonged boiling the ammonium chloride is decomposed, and re-dissolves a part of the precipitate.

Meinecke doubts this, but he concedes that on prolonged boiling the precipitated hydroxides may be converted into basic salts. Elsewhere he says that on washing a precipitate consisting of basic salts, even with warm water, they are partly decomposed, and colour the water yellow. The author's assertion that a prolonged boiling causes an error in deficiency is therefore not affected.—*Zeitschrift fur Analytische Chemie.*

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 113).

Method for the Analysis of Fermented Liquors.

A commission of experts, appointed in the year 1884 by the Chancellor of the Empire, to which was entrusted the establishment of uniform methods for the chemical investigation of wine, adopted the following resolutions, which were made public by the Prussian Minister for Commerce and Trade by a decree of the 12th August, 1884, which provides that they shall be rigidly adhered to in public institutions for the examination of food-stuffs,

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

and are recommended to the representatives of like private concerns :—

RESOLUTIONS OF THE COMMISSION FOR ESTABLISHING UNIFORM METHODS FOR THE ANALYSIS OF WINES.*

Since, in consequence of improper manner of taking, keeping, and sending in of samples of wine for investigation by the authorities, a decomposition or change in the latter often occurs, the commission consider it advisable to give the following instructions :—

Instructions for Sampling, Preserving, and Sending in of Samples of Wine for Examination by the Authorities.

1. Of each sample, at least one bottle ($\frac{3}{4}$-litre), as well filled as possible, must be taken.

2. The bottles and corks used must be perfectly clean; the best are new bottles and corks. Pitchers and opaque bottles in which the presence of impurities cannot be seen are not to be used.

3. Each bottle shall be provided with a label, gummed (not tied) on, upon which shall be given the index number of the sample corresponding to a description of it.

4. The samples are to be sent to the chemical laboratory as soon as possible to avoid any chance of alteration, which, under some circumstances, can take place in a very short time. If they are, for some special reason, retained in any other place for any length of time, the bottles are to be placed in a cellar and kept lying on their sides.

5. If in samples of wine taken from any business concern adulteration is shown, a bottle of the water is to be taken which was presumably used in the adulteration.

6. It is advisable, in many cases necessary, that, together with the wine, a copy of these resolutions be sent to the chemist.

A.—*Analytical Methods.*

Specific Gravity.—In this determination use is to be made of a picnometer, or a Westphal balance controlled by a picnometer. Temperature, 15° C.

Alcohol.—The alcohol is estimated in 50 to 100 c.c. of the wine by the distillation method. The amount of alcohol is to be given in the following way :—In 100 c.c. wine at 15° C. are contained *n* grms. alcohol. For the calculation the tables of Baumhauer or Hebner are used. (The amounts of all the other constituents are also to be given in this way; in 100 c.c. wine at 15° C. are contained *n* grms.).

Extract.—For this estimation 50 c.c. of wine, measured out at 15° C., are evaporated on the water-bath in a platinum dish (85 m.m. in diameter, 20 m.m. in height, and 75 c.c. capacity, weight about 20 grms.), and the residue heated for two and one-half hours in a water-jacket. Of wines rich in sugar (that is, wines containing over 0·5 grm. of sugar in 100 c.c.) a smaller quantity, with corresponding dilution, is taken, so that 1 or at the most 1·5 grms. extract are weighed.

Glycerin.—One hundred c.c. of wine (for sweet wines see further on) are evaporated in a roomy, not too shallow, porcelain dish to about 10 c.c., a little sand added, and milk of lime to a strong alkaline reaction, and the whole brought nearly to dryness. The residue is extracted with 50 c.c. of 96 per cent alcohol on the water-bath, with frequent stirring. The solution is poured off through a filter, and the residue exhausted by treatment with small quantities of alcohol. For this 50 to 100 c.c. are generally sufficient, so that the entire filtrate measures 100 to 200 c.c. The alcoholic solution is evaporated on the water-bath to a syrupy consistence. (The principal part of the alcohol may be distilled off if desired). The residue is taken up by 10 c.c. of absolute alcohol, mixed in a stoppered flask with 15 c.c. of ether and allowed to stand until clear, when the clear liquid is poured off into a glass-stoppered weighing-glass, filtering the last portions of the solution. The solution is then evaporated in the weighing-glass until the residue no longer flows readily, after which it is dried an hour longer in a water-jacket. After cooling it is weighed.

In the case of sweet wines (over 0·5 grm. sugar in 100 c.c.) 50 c.c. are taken in a good-sized flask, some sand added, and a sufficient quantity of powdered slack lime, and heated with frequent shaking in the water-bath. After cooling 100 c.c. of 96 per cent alcohol are added, the precipitate which forms allowed to separate, the solution filtered, and the residue washed with alcohol of the same strength. The alcoholic solution is evaporated and the residue treated as above.

Free Acids (total quantity of the acid reacting constituents of the wine).—These are to be estimated with a sufficiently dilute normal solution of alkali (at least one-third normal alkali) in 10 to 20 c.c. wine. If one-tenth normal alkali is used at least 10 c.c. of wine should be taken for titration; if one-third normal, 20 c.c. of wine. The drop method (*Tupfel methode*), with delicate reagent-paper, is recommended for the establishment of the neutral point. Any considerable quantites of carbonic acid in the wine are to be previously removed by shaking. These "free acids" are to be reckoned and reported as tartaric acid ($C_4H_6O_6$).

Volatile Acids.—These acids are to be estimated by distillation in a current of steam, and not indirectly, and reported as acetic acid ($C_2H_4O_2$). The amount of the "fixed acids" is found by subtracting from the amount of "free acids" found, the amount of tartaric acid corresponding to the "volatile acids" found.

Bitartrate of Potash and Free Tartaric Acid.—(*a*) Quantitative detection of free tartaric acid :—20 to 30 c.c. of the wine are treated with precipitated and finely-powdered bitartrate of potash, shaken repeatedly, filtered off after an hour, and 2 to 3 drops of a 20 per cent solution of acetate of potash added to the clear filtrate, and the solution allowed to stand twelve hours. The shaking and standing of the solution must take place at as nearly as possible the same temperature. If any considerable precipitate forms during this time, free tartaric acid is present, and the estimation of it and of the bitartrate of potash may be necessary.

(*b*). Quantitative estimation of the bitartrate of potash and free tartaric acid :—In two stoppered flasks two samples of 20 c.c. of wine each are treated with 200 c.c. ether-alcohol (equal volumes), after adding to the one flask 2 to 3 drops of a 20 per cent solution of acetate of potash. The mixtures are well shaken, and allowed to stand sixteen to eighteen hours at a low temperature 0—10° C.), the precipitate filtered off, washed with ether-alcohol, and titrated. (The solution of acetate of potash must be neutral, or acid. The addition of too much acetate may cause the retention of some bitartrate in solution). It is best on the score of safety to add to the filtrate from the estimation of the total tartaric acid a further portion of 2 drops of acetate of potash, to see if a further precipitation takes place.

In special cases the following procedure of Nessler and Barth may be used as a control :—

Fifty c.c. of wine are evaporated to the consistency of a thin syrup (best with the addition of quartz sand), the residue brought into a flask by means of small washings of 96 per cent alcohol, and with continual shaking more alcohol is gradually added, until the entire quantity of alcohol is about 100 c.c. The flask and contents are corked and allowed to stand four hours in a cool place, then filtered, and the precipitate washed with 96 per cent alcohol; the filter-paper, together with the partly flocculent, partly crystalline precipitate, is returned to the flask, treated with 30 c.c. warm water, titrated after cooling, and the acidity reckoned as bitartrate. The result is sometimes too high if pectinous bodies separate out in small lumps, enclosing a small portion of free acids.

In the alcoholic filtrate the alcohol is evaporated, 0·5 c.c. of a 20 per cent potassic acetate solution added,

* "Das Gesetz betreffend den Verkehr mit Nahrungsmittel," u.s.w., p. 184.

which has been acidified by a slight excess of acetic acid, and thus the formation of bitartrate from the free tartaric acid in the wine facilitated. The whole is now, like the first residue of evaporation, treated with (sand and) 96 per cent alcohol, and carefully brought into a flask, the volume of alcohol increased to 100 c.c., well shaken, corked, allowed to stand in a cold place four hours, filtered, the precipitate washed, dissolved in warm water, titrated, and for one equivalent of alkali two equivalents of tartaric acid are reckoned.

This method for the estimation of the free tartaric acid has the advantage over the former of being free from all errors of estimation by difference. The presence of considerable quantities of sulphates impairs the accuracy of the method.

Malic Acid, Succinic Acid, Citric Acid.—Methods for the separation and estimation of these acids cannot be recommended at the present time.

Salicylic Acid.—For the detection of this, 100 c.c. of wine are repeatedly shaken out with chloroform, the latter evaporated, and the aqueous solution of the residue tested with very dilute solution of ferric chloride. For the approximately quantitative determination it is sufficient to weigh the chloroform residue, after it has been again recrystallised from chloroform.

Colouring Matter.—Red wines are always to be tested for coal-tar colours. Conclusions in regard to the presence of other foreign colouring-matters drawn from the colour of precipitates and other colour reactions are only exceptionally to be regarded as safe. In the search for coal-tar colours the shaking out of 100 c.c. of the wine with ether before and after its neutralisation with ammonia is recommended. The ethereal solutions are to be tested separately.

Tannin.—In case a quantitative determination of tannin (or tannin and colouring-matter) appears necessary, the permanganate method of Neubauer is to be employed. As a rule the following estimation of the amount of tannin will suffice :—The free acids are neutralised to within 0·5 grm. in 100 c.c. with standard alkali, if necessary. Then 1 c.c. of 40 per cent sodic acetate solution is added, and drop by drop a 10 per cent solution of ferric chloride, avoiding an excess. One drop of ferric chloride is sufficient for the precipitation of 0·05 per cent of tannin. (New wines are deprived of the carbonic acid held in solution by repeated shaking).

Sugar.—The sugar should be determined, after the addition of carbonate of soda, by means of Fehling's solution, using dilute solutions, and, in wines rich in sugar, (*i.e.*, wines containing over 0·5 grm. in 100 c.c.), with observance of Soxhlet's modifications, and calculated as grape sugar. Highly coloured wines are to be decolourised with animal charcoal if their content of sugar is low, and with acetate of lead and sodium carbonate if it is high.

If the polarisation indicates the presence of cane sugar (compare under polarisation) the estimation is to be repeated in the manner indicated after the inversion (heating with hydrochloric acid) of the solution. From the difference the cane sugar can be calculated.

Polarisation.—1. With white wines :—60 c.c. of wine are treated with 3 c.c. acetate of lead solution in a graduated cylinder, and the precipitate filtered off. To 30 c.c. of the filtrate ie added 1·5 c.c. of a saturated solution of sodic carbonate, filtered again, and the filtrate polarised. This gives a dilution of 10 : 11, which must be allowed for.

2. With red wines :—60 c.c. wines are treated with 6 c.c. acetate of lead, and to 30 c.c. of the filtrate 3 c.c. of the saturated solution of sodic carbonate added, filtered again, and polarised. In this way a dilution of 5 : 6 is obtained.

The above conditions are so arranged (with white and red wines) that the last filtrate suffices to fill the 220 m.m. tube of the Wild polaristrobometer, of which the capacity is about 28 c.c.

In place of the acetate of lead very small quantities of animal charcoal can be used. In this case an addition of sodic carbonate is not necessary, nor is the volume of the wine altered. If a portion of the undiluted wine 220 m.m. long shows a higher right-handed rotation than 0·3° Wild, the following procedure is necessary :—

Two hundred and ten c.c. of the wine are evaporated on the water-bath to a thin syrup, after the addition of a few drops of a 20 per cent solution of acetate of potash. To the residue is added gradually, with continual stirring, 200 c.c. of 90 per cent alcohol. The alcoholic solution, when perfectly clear, is poured off or filtered into a flask, and the alcohol distilled or evaporated off down to about 5 c.c. The residue is treated with about 15 c.c. water and a little bone-black, filtered into a graduated cylinder, and washed with water until the filtrate measures 30 c.c. If this shows on polarisation a rotation of more than +0·5° Wild, the wine contains the unfermentable matter of commercial potato sugar (amylin). If in the estimation of the sugar by Fehling's solution more than 0·3 grm. sugar in 100 c.c. was found, the original right-rotation caused by the amylin may be diminished by the left-rotating sugar; the above precipitation with alcohol is in this case to be undertaken, even when the right-rotation is less than 0·3 Wild. The sugar is, however, first fermented by the addition of a pure yeast. With very considerable content in (Fehling's solution) reducing sugar and proportionally small left-rotation, the diminishing of the left-rotation may be brought about by cane sugar or dextrin or amylin. For the detection of the first the wine is inverted by heating with hydrochloric acid (to 50 c.c. wine, 5 c.c. dilute hydrochloric acid of specific gravity 1·10), and again polarised. If the left-rotation has increased, the presence of cane sugar is demonstrated. The presence of dextrin is shown as given in the section on "gum." In case cane sugar is present, well-washed yeast, as pure as possible, should be added, and the wine polarised after fermentation is complete. The conclusions are then the same as with the wines poor in sugar.

For polarisation only large, exact instruments are to be used.

The rotation is to be calculated in degrees Wild, according to Landolt (*Zeitschr. f. Analyt. Chemie*, vii., 9) :—

1° Wild = 4·6043° Soleil.
1° Soleil = 0·217189° Wild.
1° Wild = 2·89005° Ventzke.
1° Ventzke = 0·346015° Wild.

Gum (Arabic).—For establishing the addition of any considerable quantities of gum 4 c.c. wine are treated with 10 c.c. of 96 per cent alcohol. If gum is present the mixture becomes milky, and only clears up again after several hours. The precipitate which occurs adheres partly to the sides of the tube, and forms hard lumps. In genuine wine flakes appear after a short time, which soon settle, and remain somewhat loose. For a more exact test it is recommended to evaporate the wine to the consistency of a syrup, extract with alcohol, of the strength given above. and dissolve the insoluble residue in water. This solution is treated with some hydrochloric acid (of specific gravity 1·10) heated under pressure two hours, and the reducing power ascertained with Fehling's solution, and calculated to dextrose. In genuine wines no considerable reduction is obtained in this way. (Dextrin is to be detected in the same way).

Mannite.—As the presence of mannite in wines has been observed in a few cases, it should be considered when pointed crystals make their appearance in the extract or the glycerin.

Nitrogen.—In the estimation of nitrogen the soda-lime method is to be used.

Mineral Matters.—For this estimation 50 c.c. of wine are used. If the incineration is incomplete, the charcoal is leached with some water, and burned by itself. The solution is evaporated in the same dish, and the entire ash gently ignited.

Chlorine Estimation.—The wine is saturated with sodic

carbonate, evaporated, the residue gently ignited and exhausted with water. In this solution the chlorine is to be estimated volumetrically according to Volhard, or gravimetrically. Wines whose ashes do not burn white by gentle ignition usually contain considerable quantities of chlorine (salt).

Sulphuric Acid.—This is to be estimated directly in the wine by the addition of barium chloride. The quantitative estimation of the sulphuric acid is to be carried out only in cases where the qualitative test indicates the presence of abnormally large quantities. (In the case of viscous or very muddy wines a previous clarification with Spanish earth is to be recommended).

If in a special case it is necessary to investigate whether free sulphuric acid or potassium bisulphate are present, it must be proved that more sulphuric acid is present than is necessary to form neutral salts with all the bases.

Phosphoric Acid.—In the case of wines whose ashes do not react strongly alkaline the estimation is made by evaporating the wine with sodic carbonate and potassic nitrate, the residue gently ignited and taken up with dilute nitric acid; then the molybdenum method is to be used. If the ash reacts strongly alkaline the nitric acid solution of it can be used directly for the phosphoric acid determination.

The other mineral constituents of wine (also alum) are to be determined in the ash or residue of incineration.

Sulphurous Acid.—One hundred c.c. wine are distilled in a current of carbonic acid gas after the addition of phosphoric acid. For receiving the distillate 5 c.c. of normal iodine solution are used. After the first third has distilled off, the distillate, which must still contain an excess of free iodine, is acidified with hydrochloric acid, heated, and treated with barium chloride.

Adulteration of Grape Wine with Fruit Wine.—The detection of this adulteration can only exceptionally be carried out with certainty by means of the methods that have so far been offered. Especially are all methods untrustworthy which rely upon a single reaction to distinguish grape from fruit wine; neither is it always possible to decide with certainty from the absence of tartaric acid, or from the presence of only very small quantities, that a wine is not made from grapes.

In the manufacture of artificial wine together with water the following articles are known to be sometimes used:—Alcohol (direct, or in the shape of fortified wine), cane sugar, starch sugar, and substances rich in sugar (honey), glycerin, bitartrate of potash, tartaric acid, other vegetable acids, and substances rich in such acids, salicylic acid, mineral matters, gum arabic, tannic acid, and substances rich in the same, (*e.g.*, kino, *catechu*), foreign colouring matters, various ethers and aromas.

The estimation, or rather the means of detecting the most of these substances has been given above, with the exception of the aromas and ethers, for which no method can as yet be recommended.

The following substances may be mentioned here in particular, which serve for increasing the sugar, extract, and free acid:—Dried fruit, tamarinds, St. John's bread, dates, figs.

B.—*Rules for Judging of the Purity of Wine.*

I. (*a*). Tests and determinations which are, as a rule, to be performed in judging of the purity of wines:—Extract, alcohol, sugar, free acids as a whole, free tartaric acid qualitative, sulphuric acid, total ash, polarisation, gum, foreign colouring matters in red wines. (*b*). Tests and determinations which are also to be carried out under special circumstances:—Specific gravity, volatile acids, bitartrate of potash, and free tartaric acid quantitative, succinic acid, malic acid, citric acid, salicylic acid, sulphurous acid, tannin, mannite, special ash constituents, nitrogen.

The Commission considers it desirable, in giving the estimations generally performed, to adhere to the order of succession given above, (under (*a*).

II. The Commission cannot regard it as their province to give a guide for judging of the purity of wine, but thinks it advisable, in the light of its experience, to call attention to the following points:—

Wines which are made wholly from pure grape juice very seldom contain a less quantity of extract than 1·5 grms. in 100 c.c. wine. If wines poorer in extract occur they should be condemned, unless it can be proven that natural wines of the same district and vintage occur with a similar low content of extract.

After subtracting the "fixed acids" the remaining extract (*extractrest*) in pure wines, according to previous experience, amounts to at least 1·1 grms. in 100 c.c., and after subtracting the "free acids," at least 1 grm. Wines which show less *extractrest* are to be condemned, in case it cannot be shown that natural wines of the same district and vintage contain as small an *extractrest*.

A wine which contains appreciably more ash than 10 per cent of its extract content must contain, correspondingly, more extract than would otherwise be accepted as a minimum limit. In natural wines the relation of ash to extract approaches very closely 1 to 10 parts by weight. Still, a considerable deviation from this relation does not entirely justify the conclusion that the wine is adulterated.

The amount of free tartaric acid in pure wines, according to previous experience, does not exceed one-sixth of the entire "fixed acids."

The relation between alcohol and glycerin can vary in pure wines between 100 parts by weight of alcohol to 7 parts by weight of glycerin, and 100 parts by weight of alcohol to 14 parts by weight of glycerin. In case of wines showing a different glycerin relation, an addition of alcohol or glycerin may be inferred.

As sometimes during its handling in cellars small quantities of alcohol (at most 1 per cent by volume) may find their way into wine, this fact must be borne in mind in judging of its purity.

These proportions are not always applicable to sweet wines.

For the individual ash constituents no generally applicable limits can be given. The opinion that the better kinds of wine always contain more phosphoric acid than others is unfounded.

Wines that contain less than 0·14 grm. of mineral matter in 100 c.c. are to be condemned, if it cannot be shown that natural wines of the same kind and the same vintage, which have been subject to like treatment, have an equally small content of mineral matter.

Wines which contain more than 0·05 grm. of salt in 100 c.c. are to be condemned.

Wines that contain more than 0·092 grm. sulphuric acid (SO_3) corresponding to 0·20 grm. potassic sulphate (K_2SO_4) in 100 c.c., are to be designated as wines containing too much sulphuric acid, either from the use of gypsum or in some other way.

Through various causes wines may become viscous, black, brown, cloudy, or bitter; they may otherwise change essentially in colour, taste, and odour. The colour of red wines may also separate into a solid form; still, all these phenomena in and of themselves would not justify the condemnation of the wine as not genuine.

If during the summer-time an energetic fermentation commences in a wine, this does not justify the conclusion that an addition of sugar, or substance rich in sugar, *e.g.*, honey, &c., has taken place, for the first fermentation may have been hindered in various ways, or the wine may have had an addition of a wine rich in sugar.

The methods adopted by the "Union of Bavarian Chemists" differ considerably from the above in many particulars, so they will be given also, together with the methods adopted by the same body for the examination of beer* in somewhat condensed form.

(To be continued).

* Hilger, "Vereinbarungen u. s. w.," p. 154.

NOTICES OF BOOKS.

Report of the Commissioner of Internal Revenue for the Fiscal Year ending June 30th, 1888. Washington: Government Printing Office.

This report contains more matter of chemical interest than it might have been supposed. We have first to notice the section on methylated spirits. From experiments made, curiously enough, by the *Microscopist* to the Department, it would appear that the methylic alcohol can be extracted from methylated spirit at a profit, leaving the ethyl alcohol in such a degree of purity as to be drinkable. We are the more inclined to accept this statement, as we know that the methylated spirit supplied in this country for technical uses is not unfrequently drunk by the workman employed. In fact methyl alcohol is not a very happy agent for the "denaturation" of excisable spirit. If used in the most impure form, as Kræmer, Gerick, and Dietze suggest, it most seriously interferes with its use in a variety of manufacturing operations. We think that the German regulations are wiser in requiring not one uniform agent to be added to alcohol for whatever purpose intended, but a variety of nauseous liquids which may be used in very small quantity, such as, in certain cases, Dippel's animal oil.

A letter from the Assistant Commissioner of Inland Revenue, Canada, mentions that the methylated spirit supplied in that country contains 25 per cent of wood-spirit, and that even this mixture is furnished only under bond to varnish manufacturers and "other persons engaged in the *mechanical* (*sic* !) arts." An inferior grade, sold without bond, consists of equal parts of the two alcohols.

Considerable space is given to oleomargarine and its manufacture. This subject has been needlessly complicated in America as well as in Europe by reports that margarine butter, even though carefully prepared, was essentially injurious. Such statements are unfounded. It even happens, especially in warm climates, that margarine may remain sound and good, while natural butter becomes utterly rancid and unfit for use. All, therefore, that it is necessary for legislatures to do in this matter is to see that margarine shall be sold under its own name only, and especially that such deceitful names as butterine should be suppressed.

In this report we find descriptions of the best known methods of distinguishing between margarine and butter —none of them so absolutely decisive as it would seem desirable. An account is also given of the legislation adopted in various countries to prevent fraud in the butter trade. A useful regulation in the Russian law is that all artificial butters shall be dyed red with alkanet, a colour well adapted for this use, seeing that it is harmless, easily soluble in oily and fatty matters, and has a very high tinctorial power. The tubs or boxes in which margarine is dispatched or kept are to be stained red. Hotels, restaurants, and all public places in which food is prepared must exhibit a notice and state in their bills of fare that the dishes prepared on the premises are cooked with margarine, if such be used in their kitchens.

Proceedings of the American Pharmaceutical Association at the Thirty-sixth Annual Meeting, held at Detroit, Michigan, September, 1888; also the Constitution, Bye-laws, and Roll of Members. Philadelphia: American Pharmaceutical Association.

Among much other interesting matter we find here a discussion on a mysterious poison or reputed poison, the "Loco Weed," dreaded as a cattle poison in Colorado, New Mexico, and Kansas. It is said that horses, cows, and sheep eating this plant are first attacked with hallucinations which render them incapable of judging of the size and distance of objects. By degrees the locoed animal loses flesh, his walk becomes feeble and unsteady, the eyes are sunken and glassy, and the coat rough and lustreless. But the whole matter is involved in doubt. Three different plants, *Astragalus mollissimus*, *A. Bigelovii*, and *Oxytropis Lamberti*, each claim to be the genuine loco. On chemical investigation of *A. mollissimus* no poisonous principle was discovered, and no toxic effects were observed when extracts of the plant were administered to frogs, dogs, cats, or to human subjects. In reply to these negative results it is remarked that the experiments should have been made not on omnivorous or carnivorous animals, but upon herbivora, when different phenomena might have been observed. We may here remark that no such experiments could be made in Britain without the difficult formality of obtaining a "vivisection" license from the Home Secretary.

Further Mr. Sayre, to whom this inquiry had been entrusted, has not been able, after three years' search and after extensive journeys in the States infested by this plant, to find any unquestionable instances of poisoning of this kind. In the few cases met with the symptoms were either quite unlike those described as due to the poison, or they were capable of being referred to some other cause.

Meantime, the belief in the dangerous nature of the loco is so general that in Colorado a law has been enacted giving a record of 1½ per cent per lb. for all weed of this kind pulled up and weighed in a dried state. About 200,000 dollars have thus been already spent. As a natural consequence the *A. mollissimus* is grown for the sake of the reward, and is sent in along with a very promiscuous lot of plants, which the officials are not able to distinguish.

A paper on "Mineral Waters" contains some revelations of decided interest. One of the Continental springs is said to produce only two million bottles yearly, whilst the sales amount to eleven millions! Further, the proprietors of these springs force artificially a large volume of carbon dioxide into the water, and between the springs and the carbonating apparatus settling vats are placed in which the ferrous salts present become peroxidised and precipitated, and salt is added, as it is alleged, for the better preservation of the water.

Cream of tartar, as sold by grocers and used in baking-powders, seems to be heavily adulterated with starch, alum, and terra-alba. Sodium sulphate is also occasionally met with. One speaker in the discussion suggested that almost half the troubles of the digestive organs might be traced to the alum introduced into the stomach.

A Dictionary of Photography for the Amateur and Professional Photographer; containing Concise and Explanatory Articles; illustrated by many Specially Prepared Diagrams. By E. J. Wall. London: Hazell, Watson, and Viney, Limited.

The great number of amateur photographers who have now become quite an important interest, affords good scope for the work before us. The author, Mr. Wall, is widely and favourably known in photographic circles, and his competence as an adviser will not be called in question. In his preface he remarks that many treatises on photography are not calculated to be fully intelligible, save to persons versed in chemistry and optics. To meet this difficulty he now issues in a collected form certain articles which have already appeared in the *Amateur Photographer*. The information given in the pages before us is remarkable for its general accuracy, and only in a few comparatively unimportant instances could it be advantageously modified. In pronouncing nitric acid "extremely poisonous" the author might usefully have added "in the undiluted state," and when recommending great care in mixing sulphuric acid with water the caution might have been given to pour the acid into the water and not the water into the acid. The method of preparing

oxalic acid here given, viz., by oxidising sugar or sawdust with nitric acid, is obsolete, the action of caustic alkalies upon sawdust being now preferred. But as the photographer, be he amateur or professional, does not make his own oxalic acid, the omission is very unimportant.

The most important error which we notice is in the table of atomic weights, where platinum is given = 198 instead of 194·8, as it appears from the most recent determinations.

The table of poisons and antidotes on p. 143 is not quite trustworthy. Sodium or magnesium sulphate is safe in case of lead poisoning, but zinc sulphate is not to be advised, since, if it should not at once act as an emetic, zinc acetate would be formed in the stomach, and would prove a worse enemy than lead acetate. For potassium bichromate, magnesia and chalk would be of little use, since the magnesium and calcium chromates are not insoluble.

As proof of the extent to which photography is now practised we may mention that it has now three weekly journals, besides one monthly and two annual organs. We note also that several hotel-keepers now advertise that they have a dark room at the service of photographers.

OBITUARY.

DR. ISIDOR SOYKA.

We feel great regret in announcing the premature death of Dr. Isidor Soyka, Professor of Hygiene at the University of Prague. The deceased, who was only in his thirty-ninth year, had attained a wide and well-merited reputation by his sanitary and bacteriological studies, and especially by his bacteriological museum, in which sixty species of these microbia were shown in full activity. Prof. Soyka shot himself on February 23rd in a fit of terror at the fate of his brother, who had become insane.—*Chemiker Zeitung.*

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 8, February 25, 1889.

Remarks on the Conductivity and the Manner of Electrolysis of Concentrated Solutions of Sulphuric Acid.—E. Bouty.—The author, noting a marked change about (old notations) $SO_3 + 6HO$ or $7HO$, and again about SO_3+16HO, suggests that the former limit corresponds to the disappearance of the last trace of hydrogen peroxide, *i.e.*, the complete destruction of the hydrate SO_32HO, whilst the latter limit corresponds to the disappearance of the persulphuric acid and the destruction of an unknown hydrate.

Correction Concerning the Action of Sulphurous Acid upon the Alkaline Hyposulphites.—A. Villiers.—In the *Comptes Rendus*, vol. cvi., pp. 851 and 1354, the author describes a salt obtained by the action of sulphurous acid upon sodium hyposulphite as being a salt of a new oxy-acid of sulphur. He now finds that the product consists of the sodium trithionate and the tetrathionate.

On a Salt obtained by Saturating Phosphorous Acid with an Excess of Alkali.—L. Amat.—The crystals formed are simply disodic phosphite,—

$$P(OH)(ONa)_2+5H_2O.$$

It appears that phosphorous acid should be regarded as a bibasic acid.

On the Valence of Aluminium.—Alphonse Combes. The author recognises aluminium as trivalent.

Compound of Mannite with the Aldehyds of the Fatty Series.—J. Meunier.—Ethylic acetal, when freed from acids, forms a perfectly white mass having a slightly bluish reflection. The mass consists of fine needles melting at 174°, but which sublimes very distinctly if kept at temperatures above 10°. Under these circumstances a very small portion is decomposed.

New Neutral and Acid Ethers of the Camphols.—A. Haller.—The author examines the neutral succinates of dextro- and lævo-camphol, the racemic succinate, and the corresponding acid compounds.

Bulletin de la Société Chimique de Paris. Vol. li., No. 4.

New Apparatus for the Concentration of Extracts in Vacuo.—L. A. Adrian.—The apparatus cannot be intelligibly described without the two whole-page figures with which it is accompanied.

On the Use of Cold in the Preparation of Pharmaceutical Extracts.—L. A. Adrian.—The author's object is to effect the subsidence and consequent elimination of foreign or undesirable matter by exposure to low temperatures.

The Constitution and the Acetonic Function of Nitro-camphor.—P. Cazeneuve.

On a Hydrochlorate of Nitro-camphor. Formation of a Polymer by Hydratation, Camphortrinitro-triphenol.—P. Cazeneuve.—These two papers do not admit of useful abstraction.

Justus Liebig's Annalen der Chemie. Vol. ccl., Parts 1 and 2.

The Molecular Volumes of Liquids.—H. Kopp.—A treatise extending to 117 pages and incapable of insertion.

Researches on Aromatic Nitrites.—Here are included papers by Victor Meyer on benzylcyanide and hydratropic nitrile; by Hermann Janssen on contributions to a knowledge of the substantiability of the atoms of methylene-hydrogen in benzyl cyanide; by K. Neure on substituted benzyl cyanides, and by Howard V. Frost on the condensation of benzyl cyanide and its substitution-products with aldehyds and with amyl nitrite.

Communications from the Chemical Institute of the University of Strassburg.—A study by R. Fittig on the condensation of β-ketonic esters with bibasic acids, and including memoirs by F. von Eynern on acetacetic ester and succinic acid; by Paul Feist on the barium and calcium salts of uvic, carbuvic, and carbuvic-ethylic ester acid; by A. Dietzel on acetacetic ester and pyruvic acid; and by A. Schlœsser on benzoylacetic ester and succinic acid.

Communications from the Laboratory of Prof. Wislicenus at Leipzig.—These include papers by J. Wislicenus on the determination of the spacial position of atoms, and on other derivatives of pseudobutylene, of angelicic acid, and of tiglic acid; by O. Holz on the bromo-derivatives of pseudobutylene; by M. Pückert on the bromo addition products and the geometric configuration of angelicic and tiglic acids, and by M. Pückert on the conversion of hydro-bromo-crotonylene into monobrom-pseudobutylene.

Barium Sodium Hyposulphate.—K. Kraut.—Sodium hyposulphate, though crystrallising in different systems, form isomorphous mixtures which take the form of the sodium salt.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Iron Oxide Paint.—A correspondent wishes to know where the raw material for this paint can be obtained.

Estimation of Glycerin.—Can any of your readers direct me to a work on the estimation of glycerin in waste lye; also, what the impurities hurtful to dynamite glycerin are, and how they may be estimated?—GLYCEROL.

MEETINGS FOR THE WEEK

MONDAY, 18th.—Medical 8.30.
— Society of Arts, 8. Cantor Lectures. "The Decoration and Illustration of Books," by Walter Crane.

TUESDAY, 19th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Pathological, 8.30.
— Sanitary Institute, 8. "Drainage and Construction," by Prof. H. Robinson, M.Inst.C.E.
— Society of Arts, 8. "The Art of the Jeweller," by Carlo Giuliano.

WEDNESDAY, 20th.—Society of Arts, 8. "Objects and Methods of the Society of Arts' Motor Trials," by Prof. A. B. W. Kennedy, F.R.S.
— Meteorological, 7.
— Geological, 8.

THURSDAY, 21st.—Royal, 4.30.
— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
— Royal Society Club, 6 30.
— Institute of Electrical Engineers, 8.
— Chemical, 8. Ballot for the Election of Fellows. "The Molecular Weights of Metals," by W. Ramsay, F.R.S. "Some Compounds of Tribenzyl-phosphoric Oxide," by N. Collie.

FRIDAY, 22nd.—Royal Institution, 9. "The Science of Animal Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
— Sanitary Institute, 8. "Scavenging, Disposal o Refuse and Sewage," by H. Percy Boulnois, M.Inst.C.E.
— Quekett Club, 8.

SATURDAY, 23rd.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
— Physical, 3. "On the Use of Lissajou's Figures in the Maintenance of a Uniform Rotation," and "On the Direct Determination of the Vibration Period of a Reed or Tuning-fork by means of a Morse Receiver," by Prof. J. V. Jones. "On the Clark Cell as a Source of Standard Currents," by Prof R. Threlfall and A. Pollock. "On the Maintenance of High Specific Resistances," by Prof. R. Threlfall.

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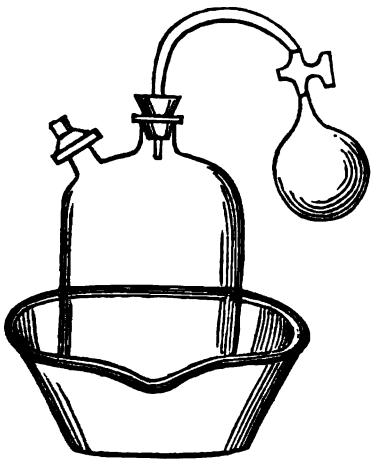
THE CHEMICAL NEWS.

Vol. LIX. No. 1530.

A SELECT METHOD OF PREPARING NITROGEN GAS.

By H. N. WARREN, Research Analyst.

The formation of nitrogen gas when required as an agent, either for the lecture-table or when in larger quantities for research, always presents more or less difficulty as regards its preparation. One process, still recorded in the various hand-books of science, being the action of nitric acid on raw meat; this method may, however, without doubt be regarded as nothing more than an alchemical memoir, since it would be evidently difficult to state, or enumerate, the complicated mixture of other gases which becoming evolved at the same time would naturally contaminate the product. The action of potassium nitrite when heated in a suitable apparatus in admixture with ammonium chloride produces, when prepared cautiously, a moderately pure gas, but owing to the inconstancy of the reaction the same is rendered considerably tedious, and unprofitable. As a third instance, the reaction that phosphorus affords when burnt in a limited supply of air, as, for instance, when confined by the aid of a bell-jar and



in direct contact with water, at once presents an elegant and at the same time uncostly method of preparing a very pure gas, and direct from the atmosphere. This, although a favourite method of most demonstrators and others when experimenting with or illustrating the component parts of the atmosphere, yet at the same time few, if any, seem to have adopted a plan to recover, or more correctly to collect, the so prepared gas, which by a slight alteration in the form of apparatus to that generally employed may be procured in any desired quantity.

The accompanying figure, which is intended to illustrate the apparatus required, consists mainly of a doubly tubulated gas-receiver or bell-jar connected either with a bladder provided with a suitable stop-cock, or, if required in larger quantities, to an ordinary gas-holder, the outer vessel containing a sufficiency of water to allow of the gas-jar at the termination of the action to be immersed to the required height. In using the apparatus all that is necessary is to apply a hot wire to the pieces of phosphorus contained in a small brass dish, the same being allowed to float upon the surface of the water. This is most readily accomplished by withdrawing the stopper from the side tubule, inserting a hot wire in order to start the combustion of the phosphorus, and replacing the stopper. The apparatus and its contents, after the combustion of the phosphorus has terminated, is allowed to remain a few moments in contact with the water in order to allow of the fumes of phosphoric pentoxide occasioned by the combustion of the phosphorus to unite with the water. The stop-cock, in connection with the receiver intended for the reception of the gas, is now opened, the weight of the bell-jar exerting a pressure sufficient to allow of its contents to be discharged into the receiver. The tap in connection with the receiver is next closed, the stopper from the side tubule again withdrawn, thus allowing on raising the apparatus to the surface of the water to admit of a fresh supply of air, which may be proceeded with as before. By this method, operating with a jar capable of retaining one cubic foot of atmosphere, a gas-holder able to contain six cubic feet of nitrogen may be filled in less than an hour.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE CHEMISTRY OF THE FLAX FIBRE.

By C. F. CROSS and E. J. BEVAN.

Flax "straw," as a matured dicotyledonous stem, is made up of wood, bast, and cortex. For the separation of the bast fibres—which constitute about 20 per cent of the weight of the stem—from wood and cortex, the well-known processes of retting and scutching are resorted to. The former, as ordinarily practised, consists in a spontaneous fermentation, set up by immersing the stems in stagnant water, which has the effect of breaking down the less resistant cellular tissue, which cements the fibres, as it were, to the wood on the one side and the cortex on the other. The scutching then thrashes out the more brittle wood, and, to a great extent, strips also the cortical tissues, leaving the textile fibre or flax, still containing residues of the wood ("sprit"), and a greater or less admixture of the cortical tissues, which have the effect of binding the fibre-bundles into ribands. Ordinary flax, therefore, is not the pure isolated bast, but, to borrow a term from the mineralogists, a concentrate; and, although the foreign or non-fibrous elements of the stem survive in very small proportion, they are of very considerable technical importance, conditioning, as they do, the very complicated bleaching treatment which flax goods, and notably linens, undergo in preparation for the white goods market.

It is a matter of common knowledge that the Mather-Kier and alkali process of treatment of the vegetable textiles have been recently introduced into Belfast, being first adopted by the firm of Fenton, Connor and Co. The results of the research, which we are about to describe in outline, have been obtained in the course of the work of developing and perfecting the process, as here applied.

The pure fibre substance is a compound of cellulose with a pectosic group. This was sufficiently established by Kolb, whose research upon its constitution is the only one with which we are acquainted (*Ann. Chim. Phys.* (4), xiv., 348). We are investigating the constitution of this non-cellulose group more closely, by means of the definite criteria which have been established by the later researches of Tollens and others (*Annalen*, ccxlix., 215—271). Amongst other results we may mention that by the action of nitric acid of 1·15 sp. gr., some quantity of mucic acid is formed; so far, however, we have not obtained of this product of decomposition more than from 1 to 2 per cent of the weight of the fibre. It should be pointed out, however, that the percentage on the non-cellulose constituent from which it is undoubtedly formed amounts to from 5 to 10. The other products of

the action of this acid are:—(*a*) Oxalic and carbonic acids —no evidence has been obtained of the formation of saccharic acid. (*b*) Fatty and wax acids, resulting from the decomposition of the cuticular substances associated with the fibre, of which we shall treat subsequently. These are dissolved by alcohol from the disintegrated fibrous residue, which is for the most part an oxycellulose, and which, after exhaustion by this solvent, is obtained comparatively pure. With regard to the yield and properties of the oxycellulose, a comparative study of pure flax and cotton celluloses revealed no sensible differences. By the action of potassium permanganate in presence of caustic soda in excess, we obtained from pure bleached linen (flax cellulose) the following products:—An oxycellulose similar to the above (45 per cent); oxalic acid (18 per cent); and a soluble carbohydrate of the aldehyd-alcohol type (15 per cent), yielding furfurol on hydrolysis by acids. The condensation of the cellulose molecule to form this aldehyd by this particular method is noteworthy.

The Wood or Sprit.—This has all the characteristics of the typical ligno-celluloses (Chemical News, lix., 106) and we have not made it the subject of special study, having devoted ourselves rather to the *Cuticular Constituents*. Hot alcohol dissolves from the scutched fibre from 2 to 3 per cent of its weight of a mixture composed of—(*a*) A wax which separates out for the most part on cooling. This appears to be a mixture of a free wax alcohol and a compound of the same alcohol with a ketone-resin. The alcohol has the composition $C_{23}H_{47}.OH$. The products of saponification were variously fractionated, but no other alcohol appears to be present. It melts at 81° to 82°. The acetate, $C_{23}H_{47}.(C_2H_3O).O$, also analysed, melts at 65°. The products of resolution of the before-mentioned "resin" are oils of indifferent properties, which are still under investigation. (*b*) In the filtrate from the crystallisation of wax (*a*) there is contained a complex of constituents, which have so far been resolved as follows:—(1) A carbohydrate of the ligno-cellulose type, but soluble in water; converted by nitric acid into a highly acid derivative, which from its properties and analysis of the calcium salt, we identify as the compound obtained by the action of nitric acid upon the ligno-celluloses and similar bodies (Chemical News, xlvii., p. 77). (2) The green semi-fused residue from the extraction of the carbohydrate by boiling water is resolved by benzene into two bodies—(*a*) a brown residue or wax, resembling in general properties the wax described under (*a*), but yielding a wax alcohol on saponification melting at 74°, and (*β*) a bright green oil, which, when deprived of the solvent and on cooling becomes semi-solid. Both (*a*) and (*β*) yield a considerable proportion of indifferent oily products of saponification, which are still under examination.

We hope shortly to complete this research, when the results will be communicated in full.

ON THE

TRUE FORMULA FOR PERMANGANATES.*

By CHARLES M. BRADBURY, of Virginia.

(Continued from p. 124).

It now remains to be shown that $KMnO_4$ is not merely a possible formula for the salt it represents, but that it is the only correct one. This I hope to do by appeal (I.) to the results of certain experiments made with reference to this question, and (II.) to facts and principles generally recognised as parts of chemical science.

* Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $R(MnO_4)_n$.

I.

(1).

If permanganates really contain two atoms of a monad base, there is no good reason why one of these may not be replaced by some other monad, thus producing a double salt. To test the possibility of producing such a salt, the following experiment was made:—

11·70 grms. of silver permanganate and 1·48 grms. potassium chloride were separately dissolved in the least quantity of hot water. The two solutions were then thoroughly mixed by shaking in a bottle with a well-ground glass stopper, and the mixture was set aside in a dark place for about twelve hours. The reaction to be expected (assuming ths correctness of the formula $\overset{I}{R}_2Mn_2O_8$) was—

$$Ag_2Mn_2O_8 + KCl = \left.\begin{matrix}K\\Ag\end{matrix}\right\} Mn_2O_8 + AgCl \quad .. \quad .. \quad (A).$$

The purple liquid was decanted from the precipitated silver chloride and placed under a bell-glass with a vessel containing strong sulphuric acid. The crystallisation occupied nearly a month. The mother-liquor was then poured off, and the small crystals were washed, dried over sulphuric acid, and analysed. The analysis gave, from 0·8120 grm. supposed double permanganate,—

Ag	0·3802
Mn	0·2025
K	0·0030

or—

		Calculated for $KAgMn_2O_8$.
Ag	46·83 per cent	28·05
Mn	24·93 ,, ,,	28·55
K	0·30 ,, ,,	10·16

So that the crystals examined were clearly not the double permanganate. Upon comparing the analysis with the calculated percentages of the elements in silver permanganate, it appears that the material was merely silver permanganate with a trace of potassium permanganate in it. The difference in solubility of the two salts readily accounts for the small proportion of the latter. Calculating the oxygen, there are found—

			Per cent.	Calculated for $Ag_2Mn_2O_8$.
Ag_2	0·3802			
O	0·0281	Ag	46·83	47·58
K_2	0·0030	Mn	24·93	24·23
O	0·0006	O	28·84	28·19
Mn_2	0·2025	K	0·31	—
O_7	0·2062			

(or)

Instead of reaction (A), the change that took place on mixing the two solutions was therefore merely—

$$2Ag_2Mn_2O_8 + 2KCl = K_2Mn_2O_8 + Ag_2Mn_2O_8 + 2AgCl,$$

or, as seems more probable,—

$$2AgMnO_4 + KCl = KMnO_4 + AgMnO_4 + AgCl.$$

(2).

An attempt was now made to prepare a double permanganate of potassium and sodium. The method first adopted was based on the suggestion that—

$$2K_2Mn_2O_8 + Na_2SO_4.10H_2O = 2\left.\begin{matrix}Na\\K\end{matrix}\right\} Mn_2O_8 + K_2SO_4 + Aq$$

ought to be a possible reaction, since potassium, being more basylous than sodium, might be expected to take sulphuric acid from that element. Hot solutions of the two salts were mixed in proper proportion, and set in a desiccator to crystallise. After ten days an abundant deposit of crystals, in general appearance reminding one of silver permanganate, was found. Upon analysis, however, they proved to be only potassium permanganate in crystals of rather unusual "habit."

			Calculated for $KMnO_4$.
K	0·2463	24·60 per cent	24·73
Mn	0·3526	35·22 ,, ,,	34·80
O (calcul.)	0·4091	40·87 ,, ,,	40·47

So that there seems to have been no chemical change of any kind.

A second trial was made on a different plan. Sodium sulphate, barium permanganate, and potassium permanganate were mixed in proportions to produce the reactions—

(1). $Na_2SO_4.10H_2O + BaMn_2O_8 = Na_2Mn_2O_8 + BaSO_4 + Aq.$

(2). $Na_2Mn_2O_8 + K_2Mn_2O_8 = 2\left\{\begin{matrix}K\\Na\end{matrix}\right\}Mn_2O_8.$

The first of these, of course, took place as soon as the solutions were mixed; but the second did not occur. After allowing the mixture to stand for some hours, the clear solution was decanted into an evaporating dish, concentrated at a gentle heat, and placed in a desiccator. Within twelve hours potassium permanganate was deposited from the solution in small prismatic crystals of the appearance, in shape and colour, so characteristic of that salt.

(3).

If potassium permanganate really contains two atoms of potassium, it ought to be possible to replace one of these by hydrogen, thus forming an acid salt. Accordingly five grms. of potassium permanganate was dissolved, and treated with a quantity of hydrofluosilicic acid corresponding to one-half the potassium. The potassium silicofluoride was caught on an asbestos filter, and the filtrate concentrated over sulphuric acid. After a few days sufficient crystals were deposited for examination. They did not differ in appearance from many specimens of potassium permanganate, and upon attempting to determine water in 0·8193 grm., none was found. Hence the substance contained no hydrogen, and was, in fact, merely re-crystallised potassium permanganate.

(4).

The untrustworthy character of the only description accessible to me of the "acid permanganate of baryta" alleged by some to exist, has already been alluded to. As it would be unreasonable to reject assertions, which if true ought to be so easy to prove, without testing them by experiment, I endeavoured to prepare some of these crystals. An accurately weighed portion of barium permanganate was dissolved, and treated with just the amount of normal solution of sulphuric acid necessary, theoretically, to precipitate all the barium. After a couple of hours the clear solution was decanted and evaporated on a water-bath at a very gentle heat. When quite concentrated it was allowed to cool, but yielded no crystals of any kind, nor did further evaporation produce any; the final product was a black powder insoluble in water—MnO_2. A second portion of barium permanganate was now dissolved and treated in the same way, except that rather less sulphuric acid was purposely used than would precipitate all of the barium. But not even this, in which the conditions for forming an acid barium permanganate (if it can exist) were almost certainly present, yielded, on gradual evaporation, anything but a crust of manganic oxide and a little barium permanganate.

(5).

While it might be desirable to multiply experiments like those already described, which bear directly upon the question at issue, so as still further to reduce the chance of error in drawing a conclusion, circumstances have prevented this. But before passing on to further theoretical reasons (which are very strong) for receiving the monobasic formula, it may be well to describe a few other practical tests that have a less direct, but scarcely less important, bearing on the subject.

The arguments to be used in II. are largely dependent upon the isomorphism of the permanganates with the perchlorates. The *fact* can scarcely be questioned, as it seems to be recognised by all authorities. As opinions appear to differ as to its degree, an endeavour was made to determine this.

Several attempts were made to establish the exact isomorphism of potassium permanganate and potassium perchlorate according to the rule proposed by Kopp, that the test of strict isomorphism should be the growth of crystals of one of the substances, when suspended in a saturated solution of the other. This was found to be impracticable. Crystals of permanganate suspended in a saturated solution of perchlorate in every case dissolved entirely, and crystals of perchlorate, while easily coated or stained with permanganate, did not have the appearance of having grown, in a crystallographic sense.

There was no difficulty, however, in getting the salts to crystallise together, the crystals of the mixture being in some cases remarkably perfect in shape and beautiful in colour, varying according to the proportions of the constituents when examined with a lens.

Twelve different mixtures were prepared, six as nearly as possible in varying integral proportions—as one to two, one to three, five to one—the remainder being mixtures of accurately weighed portions of the salts, without any attempt at exact proportion. These were dissolved in hot water and left to evaporate in the air, loosely covered with filter-paper to exclude dust.

The result was in each case a mass of minute crystals, with every indication in colour, shape, and size, of being mixtures of permanganate and perchlorate. One or two of the solutions, which were allowed to evaporate to dryness, yielded what seemed to be two kinds of crystals, a lighter and a darker. The others gave crystals which, when drained, washed, and dried, had the appearance of being the same throughout, and were often, as before remarked, exceedingly well developed.

In no single instance, however, did analysis of these crystals indicate the proportions of permanganate and perchlorate that had been used in making them. In all of the analyses* that I considered most trustworthy (the amount of material taken was in most cases smaller than would have been desirable for accuracy), more perchlorate was found than was expected—often largely more—and less permanganate. As this excess was quite balanced by deficiency of the manganese, and was found even when especial care had been taken to exclude chlorine from any other source than the salt under examination, it must be accounted for otherwise than by supposing repeated error in the analyses. Two considerations at least would lead one to expect results similar to those found; first, that the perchlorate is the less soluble of the two salts, and would therefore crystallise in advance of the other; second, that the solution of permanganate is liable to decomposition when exposed to the air, while the perchlorate is stable.

As examples of this variation, I will give the results of analysis of specimens 7 and 8: Eighty-five m.grms. of No. 7 ought to have given, according to the proportions used in making the solution (0·7309 grm. permanganate to 0·3012 perchlorate), 25 m.grms. perchlorate and 60 m.grms. permanganate. The actual result was—

Grm.	Grm.
Instead of 0·025	0·070 perchlorate.
,, ,, 0·060	0·013 permanganate.
0·085	0·083

* The method used with the first six samples was to ignite with excess of alkaline carbonate, dissolve the fused mass in water, acidify with nitric acid, and precipitate chlorine with silver nitrate. The silver chloride was caught on a filter, washed, the excess of silver nitrate removed from the filtrate by adding hydrochloric acid and again filtering, and the filtrate finally treated with ammonia and bromine to precipitate manganese. The other six were treated similarly, except that the manganese was precipitated first from the alkaline solution with hydrogen dioxide.

These crystals were well formed but small, not more than half a m.m. thick. Under the lens they appeared translucent, with a beautiful crimson colour.

No. 8 was in crystals so minute that to the naked eye they appeared as a purple red crystalline powder. The lens, however, revealed that the crystals were as well formed individually as No. 7, and that their colour by transmitted light was a rather faint red. The solution from which these separated had been made of 1·6814 grm. perchlorate and 0·3261 grm. permanganate. The 148 m.grms. used in analysis should have contained, therefore, 124 m.grms. of perchlorate and 24 of permanganate. The result was—

Grm.		Grm.	
Instead of	0·024	0·011	permanganate.
,, ,,	0·124	0·138	perchlorate.
	0·148		0·149

The results, on the whole, agree with the statement usually made, that these two salts are isomorphous to the extent of crystallising together in all proportions. Hence the right to make deductions from this isomorphism cannot be doubted.

II.

If it were possible to ascertain the vapour density of potassium permanganate, there would be no difficulty in choosing between the formula $KMnO_4$ and $K_2Mn_2O_8$, as, according to the law of Avogadro, the molecular weight of the compound would thereby be decided. But since this is impracticable, owing to the decomposition of the salt at a temperature as low as 240° C.,* the problem must be attacked by methods less direct.

It is assumed that the received formula for the perchlorates, $R(ClO_4)_n$, is correct. Granting this, it follows almost necessarily that the permanganates are represented by the analogous formula $R(MnO_4)_n$, from the following considerations.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, March 7th, 1889.

SIR,—We submit herewith the results of our analyses of the 166 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 166 samples examined, three were recorded as "very slightly turbid."

The water supplied to the metropolis during the past month, despite the unfavourable state of the weather and frequent prevalence of frost and heavy snow, continued to be of excellent quality; and its variation in mean composition, as compared with that of the previous month's supply, though not indeed of any significance, was in the direction of an increased degree of freedom from organic matter.

It may be well to re-state on this occasion that our estimate of the degree of freedom of the water from organic matter is based mainly on the concordance of two sets of determinations, namely, a daily determination, by means of permanganate of potash, of the weight of oxygen expended in the oxidation of the organic matter present in a daily collected sample of each Company's supply; and in a weekly determination, by the combustion process, of the weight of organic carbon present in a weekly sample of each Company's supply, collected on some one day during the week.

In this way the mean weights of oxygen expended in the oxidation of the organic matter present, per gallon, in the Thames-derived water in the months of January and February, were found to be 0·062 and 0·056 grain respectively; while the mean amounts of organic carbon present in 100,000 parts of the water were found to be 0·170 and 0·161 part respectively. The maximum amount found in any of the samples examined in February, or 0·173 part in 100,000 parts of the water, corresponds, as nearly as may be, to about one-third of a grain of organic matter per gallon.

In the case of the East London Company's water, the mean weight of oxygen absorbed from the permanganate was found to be 0·045 grain per gallon; and the mean amount of organic carbon was found to be 0·145 part in 100,000 parts.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

* R. and S., II., ii., 22.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Continued from p. 131).

WINES.

Methods of Investigation.

I. *Determination of Specific Gravity.*—This is to be done by means of a Westphal's balance or a picnometer, and always at 15° C.

II. *Determination of Extract.*—10 to 50 c.c. wine at 15° C. are evaporated in a platinum dish on the water-bath to the proper consistence, and then dried in a drying-oven at 100° C. to constant loss of weight. Constant loss of weight is assumed when three weighings, with equal intervals between the first and second and second and third, give equal differences between the successive weighings.

Weighings are to be made at intervals of fifteen minutes.

III. *Inorganic Matter.*—This is the incombustible ash obtained by burning the extract. Repeated moistening,

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

drying, and heating to redness are advisable to entirely get rid of all organic constituents.

IV. *Acidity.*—After shaking vigorously, to drive off carbonic acid, the wine is to be titrated with an alkali solution and the acidity expressed in terms of tartaric acid.

V. *Glycerin.*—(1). This is determined in dry wines as follows:—The alcohol is driven off from 100 c.c. wine, lime or magnesia added, and the mass evaporated to dryness. The residue is boiled with 90 per cent alcohol, filtered, and the filtrate evaporated to dryness. This residue is dissolved in 10 to 20 c.c. alcohol, 15 to 30 c.c. ether added, and the mixture allowed to stand until it is clear. It is then decanted from the sticky precipitate into a glass-stoppered weighing-bottle, evaporated to constant loss of weight, and weighed.

(2). The following method is employed for sweet wines:—One hundred c.c. wine are measured into a porcelain dish and evaporated on the water-bath to a syrupy consistence, mixed with 100 to 150 c.c. absolute alcohol, poured into a flask, ether added in the proportion of 1½ volumes to each volume of alcohol used, the flask well shaken, and allowed to stand until the liquid becomes clear. This is then poured off and the residue again treated with a mixture of alcohol and ether. The liquids are mixed, the alcohol and ether driven off, the residue dissolved in water, and treated as in (1).

(3). In all glycerin determinations it is necessary to take into consideration the loss of glycerin due to its volatility with water and alcohol vapour, and accordingly to add to the glycerin found 0·100 grm. for each 100 c.c. of liquid evaporated.

(4). It is necessary to test the glycerin from sweet wines for sugar, and if any is present it must be estimated by Soxhlet's or Knapp's method and its weight subtracted from that of the glycerin.

VI. *Alcohol.*—The determination must be made by distillation in glass vessels, and the results stated as follows:—One hundred c.c. wine at 15° C. contain x grms. or c.c. alcohol.

VII. *Polarisation.*—(1). The wine is decolourised with plumbic subacetate.

(2). A slight excess of sodic carbonate is added to the filtrate from (1). 2 c.c. of a solution of plumbic subacetate are added to 40 c.c. white wine, and 5 c.c. to 40 c.c. red wine, the solution is filtered and 1 c.c. of a saturated solution of sodic carbonate added to 21 or 22·5 c.c. of the filtrate.

(3). The kind of apparatus used and the length of the tube are to be given, and results estimated in equivalents of Wild's polaristrobometer with 200-m.m. tubes.

(4). All samples rotating more than 0·5 degree to the right (in 220-m.m. tubes, after treating as above), and showing no change, or but little change, in their rotatory power after inversion, are to be considered as containing unfermented glucose (starch sugar) residue.

(5). Rotatory power of less than 0·3 degree to the right shows that impure glucose has not been added.

(7). Wines rotating between 0·3 degree and 0·5 degree to the right must be treated by the alcohol method.

(7). Wines rotating strongly to the left must be fermented and their optical properties then examined.

VIII. *Sugar.*—This is to be determined by Soxhlet's or Knapp's method. The presence of unfermented cane sugar is to be shown by inversion, &c.

IX. *Potassic Bitartrate.*—The determination of potassic bitartrate as such is to be omitted.

X. *Tartaric, Malic, and Succinic Acids.*—(1). According to Schmidt and Hiepe's method.

(2). Determination of tartaric acid according to the modified Berthelot-Fleury method.

(3). If the addition of 1 grm. finely-powdered tartaric acid to 100 grms. wine produces no precipitate of potassic bitartrate, the modified Berthelot-Fleury method must be employed to determine free tartaric acid.

XI. *Colouring Method.*—(1). Only aniline dyes are to be looked for.

(2). Special attention is to be paid to the spectroscopic behaviour of the rosaniline dyes, as obtained by shaking wines with amyl alcohol before and after saturation with ammonia.

(3). A qualitative test for alumina is not sufficient evidence of the addition of alum.

XII. *Nitrogen.*—To be determined according to the ordinary method.

XIII. *Citric Acid.*—Presence to be shown by a qualitative test, as baric citrate.

XIV. *Sulphuric Acid.*—To be determined in the wine after adding hydrochloric acid.

XV. *Chlorine.*—To be determined in the nitric acid solution of the burnt residue by Volhard's method.

XVI. *Lime, Magnesia, and Phosphoric Acid.*—These are determined in the ash fused with sodic hydrate and potassic nitrate, the phosphoric acid by the molybdenum method.

XVII. *Potash.*—Either in the wine ash, as the platinum double salt, or in the wine itself, by Kayser's method.

XVIII. *Gums.*—Presence shown by precipitation by alcohol; 4 c.c. wine and 10 c.c. 96 per cent alcohol are mixed. If gum arabic has been added, a lumpy, thick, stringy precipitate is produced; whereas pure wine becomes at first opalescent and then flocculent.

Methods of Judging Purity—(Burtheilung).

Part I.

I. Commercial wines may be defined as follows:—(*a*). The product obtained by the fermentation of grape juice with or without grape skins and stems. (*b*). The product obtained by the fermentation of pure must, to which pure sugar, water, or infusion of grape skins has been added. It must contain not more than 9 per cent alcohol and 0·3 per cent sugar, and not less than 0·7 per cent acid, estimated as tartaric. (*c*). The product obtained in southern countries by the addition of alcohol to fermented or partly fermented grape juice. French wines are not included, however. (*d*). The product obtained by fermenting the expressed juice of more or less completely dried wine-grapes.

II. The above definitions do not apply to champagnes.

III. The following include the operations undergone by wines in cellars (*Kellermässige Behandlung*):—(*a*). Drawing and filling. (*b*). Filtration. (*c*). Clarification by the use of kaolin, isinglass, gelatin, or albumen, with or without tannin. (*d*). Sulphuring. Only minute traces of sulphurous acid may be contained in wine for consumption. (*e*). Adulteration of wine. (*f*). Addition of alcohol to wine intended for export.

IV. Wines, even if plastered, must not contain more sulphuric acid than that corresponding to 2 grms. potassic sulphate (K_2SO_4) per litre.

V. Medicinal wines are those mentioned in Parts I. and IV., with the following restrictions:—(*a*). They must not contain more sulphuric acid than corresponds to 1 grm. potassic sulphate per litre. (*b*). They must contain no sulphurous acid. (*c*). The percentage of alcohol and sugar to be given on the label. (*d*). These restrictions apply only to wines expressly recommended or sold for medicinal use.

Part II.

I. Improperly gallised wines are preparations of grape juice, pure sugar, and water, or grape-skin infusion, that contain more than 9 per cent alcohol or less than 0·7 per cent acid, or both, and preparations in which impure glucose has been used. The following facts enable us to detect them:—Small quantities of inorganic matter (phosphoric acid and magnesia), and right rotation if impure glucose is used. If the rotation exceeds 0·2° to the right, the wine is to be concentrated, freed from tartaric acid as far as possible, and again polarised.

II. Addition of alcohol is to be assumed if the ratio of alcohol to glycerin is greater than 10 to 1 by weight.

III. Addition of water and alcohol is recognised by the diminution in the quantity of inorganic matter, especially magnesia, phosphoric acid, and usually potash. Addition of water alone is recognised in the same way.

IV. Scheelisation, *i.e.*, addition of glycerin, is assumed if the ratio of glycerin to alcohol exceeds 1 to 6 by weight.

V. The presence of cane sugar is ascertained by a determination of sugar (by Soxhlet's or Knapp's method), before and after inversion.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

Messrs. P. Norman Evans, Percy A. E. Richards, and Thomas J. Underhill were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick William Boam, 2, De Montford Square, Leicester; William Frew, King James Place, Perth; James Hall, Grove House, Tottenham; James Bruce Miller, Rubislaw, Den North, Aberdeen; George Cannon McMurtry, 35, Binfield Road, Clapham, S.W.; John Charles Platts, 25, Harcourt Road, Crookesmoor, Sheffield; Duncan Taylor Richards, 12, Park Terrace, South Shields; John William Slater, 36, Wray Crescent, Tollington Park, N.; William John Waterhouse, 211, Lord Street, Southport; Mortimer Woolf, 3, Acoll Road, West Hampstead.

The following papers were read:—

23. "*The Decomposition of Carbon Disulphide by Shock; a Lecture Experiment.*" By T. E. Thorpe, F.R.S.

The author, in studying the action of the fluid alloy of potassium and sodium on carbon disulphide, obtained a yellowish brown solid substance which exploded with great violence when subjected to pressure or friction. If the explosion occurred in contact with carbon disulphide that substance was resolved into its elements.

As carbon disulphide is an endothermic compound the author was induced to try whether its vapour could not be resolved into its elements by the explosion of various detonating agents, *e.g.*, mercuric fulminate, in the manner indicated by Berthelot. It is found that such a decomposition is readily effected by exploding a charge of 0·05 grm. fulminate within a stout glass tube containing a few c.c. of carbon disulphide vapour. The carbon disulphide is at once resolved into carbon and sulphur, which line the inside of the tube. The experiment may be easily made with perfect safety, and forms a good illustration, for class purposes, of the resolution of an endothermic substance into its elements by sudden shock.

Discussion.

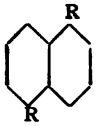
The President pointed out that the spectrum of mercury was rich in ultra violet rays, and suggested that perhaps the decomposition was induced by these rays.

Professor Thorpe, in reply, said that this explanation had not occurred to him; he believed, however, that the effect was purely mechanical, inasmuch as Berthelot had, in fact, exploded nitrous oxide by sudden compression. In reply to Mr. Groves, he said that he had only experimented with the gaseous disulphide; he believed that no explosive compound was formed by treating the disulphide with sodium.

24. "*The Determination of the Constitution of the Heteronucleal αβ- and ββ-di-derivatives of Naphthalene.*" By Henry E. Armstrong and W. P. Wynne.

In a recent communication (*Chem. Soc. Proceedings*, No. 58, 1888, p. 104) the authors have shown that proof has now been obtained that the two dichloronaphthalenes melting at 48° and 63·5° corresponding respectively to the Dahl and Badische modifications of betanaphthylaminesulphonic acid, are the 1 : 2′ and 1 : 3′ *heteronucleal* cichloronaphthalenes; at the same time they have insisted that it is impossible from existing data to determine whether the compound melting at 48° is the 1 : 2′, and that melting at 63·5° the 1 : 3′-derivative or *vice versâ*, and this they have done notwithstanding the evidence brought forward by Erdmann and Kirchhoff (*Annalen*, ccxlvii, 366; *Berichte*, 1888, 3447; *Chem. Soc. Proceedings*, No. 61, 1889, p. 8). These chemists have inferred that the dichloronaphthalene melting at 48° is the 1 : 3′-derivative, as they prepared it synthetically from metachlorobenzaldehyd; and they regard the isomeride which the authors have shown melts at 63·5° as the 1 : 2′-derivative, as they obtained it from parachlorobenzaldhyd. The authors have on several occasions criticised Erdmann and Kirchhoff's arguments and have pointed out their insufficiency, their main objection being that the position of the hydroxyl in the naphthol-derivatives prepared synthetically could not be determined; they have also suggested that in some cases the hydroxyl might take up the position indicated by Erdmann and Kirchhoff, and in others the alternative alpha-position. Moreover, it appears to them that the argument recently advanced by Erdmann (*Berichte*, 1888, 3447), in reply to their criticism, is deprived of its force by Erdmann's own admission that phenylisocrotonic acid is converted with exceptional ease into the corresponding lactone; however stable the lactone may be when formed, the fact that it is so readily producible is indicative of the manner in which the naphthol-hydroxyl might eventually assume a different position from that assigned to it by Erdmann. And even if no argument of this kind could be advanced, the fact that condensation is effected at a relatively high temperature and that it involves considerable molecular rearrangement, renders the occurrence of isomeric change both possible and probable.

Believing that, "as in the case of benzene there is little doubt that the constitution of naphthalene-derivatives will be determined eventually by the study of naphthalene-derivatives and not by synthetic methods of the character of those of Erdmann and Kirchhoff" (*Brit. Assoc. Rep.*, 1888; Chem. News., lviii., 295), they have devoted their attention to the study of the chloronaphthylaminesulphonic acids: by determining the relative positions of the three pairs of radicles Cl and NH_2, Cl and SO_3H, and NH_2 and SO_3H, in such acids, it is obviously possible to determine the relative positions of the three radicles in a heteronucleal chloramidosulphonic acid, and on this result the absolute orientation of the radicles may be based, *provided* that it can be shown how the radicles are situated in any one of the two pairs of hetero-di-derivatives obtainable from the tri-derivative. No absolute method, free from reproach, has yet been devised of determining the constitution of any known hetero-di-derivative of naphthalene, but in the case of the *αα*-compounds, arguments may be advanced which are of such weight as to leave but little room for doubt. The two possible hetero-*αα*-compounds are represented by the symbols—



I.

II.

There can be little doubt, and it is indeed generally held, that so-called *α*-dinitronaphthalene (m. p. = 216°) and the corresponding *γ*-dichloronaphthalene (m. p. = 107°) are compounds of type I., and that *β*-dinitronaphthalene (m. p. = 170°) and the corresponding *ζ*-dichloronaphthalene

(m. p. = 83°) are compounds of type II. Thus, β-diamidonaphthalene, according to Aguiar's observations on its behaviour towards nitrous acid and towards oxalates (*Ber.*, 1874, 313), behaves in an altogether peculiar manner, simulating that of an ortho-di-derivative, as pointed out originally by Ladenburg (*ibid.*, 1878, 1651). The pseudortho character of β-diamidonaphthalene and the corresponding di-derivatives is also established by Ekstrand's investigation of the nitronaphthoic acid corresponding to β-dinitronaphthalene (*ibid.*, 1883, 2881); by Bamberger's investigation of naphthalic acid (*ibid.*, 1887, 237); and by Erdmann's investigation of the α-amido-α-sulphonic acid obtained on reducing the so-called Schöllkopf α-nitronaphthalene-α-sulphonic acid (*Annalen*, ccxlvii., 343). On the other hand, an argument of great force in favour of the adoption of a formula of type I. for α-dinitronaphthalene and other corresponding uniform di-derivatives (derivatives containing two similar radicles) may be derived from the fact that all melt at higher temperatures than the isomeric αα-compounds; it is to be expected, on general grounds, that compounds of symmetrical structure would be thus distinguished.

By sulphonating 1 : 2 α-chloro-β-naphthylamine hydrochloride by means of four times its weight of an acid containing about 2 per cent of SO_3, the authors haves succeeded in obtaining three isomeric α-chloro-β-amidosulphonic acids. No. I. acid is produced in largest amount and almost exclusively if sulphonation be effected by heating at 70° for six hours. If the heating be prolonged for about six hours at a somewhat higher temperature, viz., about 100°, No. II. acid is the chief product. No. III. acid is chiefly produced if sulphonation be effected by heating during about six hours at about 160°. No. I. acid is very difficultly soluble in water; it is best purified by dissolving it as sodium salt in a large bulk of boiling hot water and precipitating by acid; the separated acid is at once filtered off, and these operations are several times repeated. It usually crystallises is glistening, flat, elongated prisms; its salts crystallise well, but are easily soluble, especially the sodium and ammonium salts. No. II. acid is slightly more soluble than the No. I. acid, and crystallises in a less characteristic manner; its salts are difficultly soluble; the sodium salt is especially characteristic, being almost insoluble in the presence of alkali; it crystallises with $4\frac{1}{2}$ mols. H_2O in glistening, apparently monoclinic plates. No. III. acid is the most soluble, and yields very soluble salts, which do not crystallise well; it crystallises in tufts of needles. This acid is best separated from No. II. acid by means of the ammonium or sodium salts.

In order to determine the constitution of these acids the authors have, on the one hand, displaced the halogen by means of sodium amalgam, and, on the other, have displaced the β-amido-group by means of v. Baeyer's hydrazine method. They have already ascertained that the No. I. acid affords the Dahl modification of betanaphthylamine sulphonic acid, and the No. III. acid the so-called δ-acid of Bayer and Duisberg; the investigation of the amido-acid from No. II. acid, and of the three chlorosulphonic acids derived from the three chloramidosulphonic acids is also almost completed.

In the number of the *Chemiker Zeitung* just to hand, mention is made of the title of a paper by P. Hellström, read at the Swedish Academy of Sciences on February 13th, from which it appears that the same subject is elsewhere being investigated, and it is on this ground alone that the authors are induced to communicate their results in the present incomplete form.

There is little doubt that under ordinary conditions of sulphodation chlorobetanaphthylamine will yield other products than those described, and in fact others have already been observed. The authors propose also to study the sulphonic acids obtained from other chloronaphthylamines, and have, in fact, already prepared acids from dichloralphanaphthylamine from 1 : 2 chloralphanaphthylamine and from bromalphanaphthylamine. It is anticipated that in this way it will be possible to determine the constitution of the dichloronaphthalenesulphonic acids, and hence to determine the manner in which substitution is effected in their formation. From their No. 1 chloramidosulphonic acid the authors have already prepared the corresponding dichloronaphthalenesulphonic acid, and find that it is identical with the chief product of the sulphonation of the 1 : 2 dichloronaphthalene melting at 34°, that, namely, which yields a sulphochloride crystallising in massive prisms melting at about 105° (*Brit. Ass. Report*, 1888; CHEMICAL NEWS, lviii., 296).

25. "*The Action of Chloroform and Alcoholic Potash on Phenylhydrazine.*" By S. RUHEMANN, Ph.D., M.A.

The author finds that together with the compound previously described by Mr. Elliot and himself (*Chem. Soc. Trans.*, 1888, 850), which he proposes to call *diisocyananilide*, there is formed a certain amount of formylphenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}COH$. From paratolylhydrazine, in like manner, he has obtained formylparatolylhydrazine and diisocyanparatoluidide; the latter crystallises in faintly yellow plates, melting at 185°.

Diisocyananilide is converted by the action of methyl iodide into a methammonium iodide of the formula $C_{14}H_{11}N_4(CH_3).CH_3I$, the production of which is proof of the presence of an imido-group. On adding bromine to an acetic solution of the anilide, a mixture of a monobromo- (m.p. 220°) and a tribromo-derivative is precipitated; the solution containing a third substance (m. p. 131°) of the formula $C_{14}H_{10}Br_2N_4$.

The Anniversary Meeting will be held on Thursday, March 28th, at 8 p.m., when the President will deliver an Address on "Recent Researches on the Rare Earths as Interpreted by the Spectroscope."

PHYSICAL SOCIETY.

March 9, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

PROF. R. THRELFALL and Prof. A. S. Herschel were elected Members of the Society.

Prof. O. LODGE read a paper "*On Magneto-optic Rotation by Transient Currents, with Reference to the Time required for the Production of the Effect.*"

If a piece of heavy glass or tube of carbon bisulphide be placed between two crossed Nicols and surrounded by a solenoid, light passes through when a Leyden jar is discharged through the wire. That the discharge is oscillatory may be proved by turning the analyser slightly to one side or the other, this having no effect on the result, or the beam may be examined by a revolving mirror, in which case a beaded band is seen when the discharge takes place. When the spark itself is analysed in the same way a serrated band results. The frequency of the oscillations being given by the formula—

$$n = \frac{1}{2\pi\sqrt{LS}\sqrt{\mu K}}$$

it is evident that n will be decreased by increasing the capacity, S, and self-induction, L, and this fact was demonstrated by connecting two condensers, first in series and then in parallel, and placing coils of wire in the circuit. The pitch of the sound emitted by the spark was by these means brought within the musical scale. Contrary to expectation, the insertion of a coil with an iron core produced little or no change in the pitch, the reason given being that the induced currents in the skin of the iron wire, due to such rapid oscillations of current, prevents the interior being magnetised. From the mathematical theory of the brightening of the dark field

it appears that the relative brightness, B, when compared with the light field obtained from the uncrossed Nicols is given by—

$$B = \frac{1}{\tau}\int_0^{\tau} \sin^2\theta\, dt,$$

where τ is the time during which an impression can be accumulated on the retina and θ the angle through which the polarised beam is rotated. When θ is considered small—

$$B = 16\pi^2 k^2 n^2 . \frac{\frac{1}{2}SV_o^2}{R\tau},$$

where k = Verdet's constant, n = number of convolutions on the solenoid, R = resistance of circuit, and $\frac{1}{2}SV_o^2$ the initial energy of the static charge. The general solution is given as—

$$B = \frac{1}{2m\tau}\int_0^{A} \frac{1 - J_o(x)}{x}\, dx,$$

where $m = \frac{R}{2L}$, $A = 8\pi k n \mu V_o \sqrt{\frac{S}{L}}$ and $J_o(x)$ Bessel function.

Taking the approximate solution, the question as to what is the best size of wire wherewith to wind the solenoid is considered, and as the insulation is very important it is concluded that the secondary of a Ruhmkorff coil is very suitable. The main interest of the experiment is said to lie in the evidence afforded of the practical instantaneity of the development of the rotary property in the substance under examination, for Villari (from experiments made on a glass drum revolving in a magnetic field) inferred that a distinct time between 1-800th and 1-400th of a second was necessary, whereas Prof. Bichat and Blondlot of Nancy, have concluded that the time required is less than 1-30,000th second. The author finds that carbon bisulphide is able to show the effect when the rate of alternation is 70,000 per second, and has no reason to believe that glass is in any way inferior. As a possible explanation of Villari's results he suggests that the strain due to centrifugal force would modify the components of the polarised beam and produce elliptic polarisation.

Mr. WARD mentioned that experiments similar to Villari's were now being carried out at the Cavendish Laboratory, a disc of glass being rotated about 200 times per second by means of a turbine. The results so far obtained do not confirm Villari's, but owing to difficulties in keeping the speed constant it is impossible to make exact measurements. It has, however, been found that the strain due to centrifugal force rotates the plane of polarisation, and elliptically polarises the beam, and that passing an alternate current round a stationary glass bar produces a distinct rotation of polarised light passing through it.

Referring to the oscillatory discharge of a jar, Prof. RÜCKER directed attention to Dr. E. Cook's experiments, described before the Society in June, 1888, when photographs showing the dust figures produced by sparks were exhibited, and pointed out that the frequency required to produce air waves of the length there indicated was of the same order as the rate of oscillatory discharge, viz., about one million per second. Prof. Rücker also wished to know whether glass behaved precisely like CS_2.

Dr. LODGE said his experiments were not exact enough to decide the latter question, and mentioned that Mr. Chattock had some time ago produced dust figures in tubes by jar discharges, and shown that the wave-length depended on the capacity and self-induction.

Prof. AYRTON suggested the use of a phonograph as a means of recording and reproducing the oscillations, in the same way as himself and Prof. Perry have analysed the current curves of alternating dynamos. The discharge could be passed through a small coil fixed to a diaphragm, and placed near a coil through which a steady current was passing, the attractions and repulsions serrating the surface of the rapidly revolving cylinder. By means of a mirror attached to a delicate magnifying spring the section of the surface may be determined. He also enquired whether the experiments shown do prove that the effect is instantaneous.

Dr. THOMPSON remarked that it was satisfactory to learn that Villari's results admit of an interpretation other than by time effect, and thought it advisable to vary the experiment by rotating a bar of glass, but Mr. WARD said he attempted that experiment four years ago and abandoned it on account of the enormous speed required.

DR. LODGE showed "Some Experiments allied to those of Hertz," and pointed out that all the effects were due to resonance. The plates of an air condenser were connected by a wire loop and placed near a Holtz machine in action. On adjusting the distance between the plates to a particular value, sparks were observed to pass between them, but on increasing or decreasing that distance the sparks ceased. It was also shown that the sparking was interrupted if the connecting loop was replaced by a coil, though the coil was effective when connected to a condenser of smaller size, thus demonstrating that the time constant of the condenser circuit was all important. Another important condition to be observed in such experiments is that the receiving circuit must be closed except at the sparking place, so as to permit the surgings of electricity to take place freely.

Other experiments were shown in which two spheres provided with rods terminating in knobs were used as a Hertz's oscillator, and sparks could be obtained from straight pieces of wire of suitable length held at some distance from the spheres.

Dr. LODGE remarked that sparks could be obtained from almost any scrap of wire or metal in close proximity to an induction coil and oscillator, but to produce the effects at considerable distances careful timing of the receiving circuit was necessary.

The author also described the results of some experiments on the velocity with which electric waves travel along wires, and concluded (contrary to Hertz) that this was not greatly different from the velocity of light.

Owing to the late hour the other papers announced to be read were postponed.

NOTICES OF BOOKS.

Report on the Cost and Efficiency of the Heating and Ventilation of Schools, for the Use and by the Request of the School Board of Dundee. By THOMAS CARNELLEY, D.Sc., F.C.S. Dundee: Winter, Duncan, and Co.

WE have here a very elaborate and useful investigation on an important point in the working of schools. Some of the facts here brought to light are surprising. The consumption of coal per head varies excessively in different towns. Thus, in Dundee and Aberdeen it is 42 lbs. per head, whilst in Nottingham, with a milder climate, it reaches 195 lbs. Hence, as Dr. Carnelley puts it, "either the children are being comparatively frozen in Dundee and Aberdeen, or they are being roasted in Leeds and Nottingham." In Dundee one fire is allotted for 80 scholars, whilst in many towns the allowance is one for 60.

This difference does not depend, as we might think, on the nature of the heating-apparatus, whether open fires, stoves, large hot-water pipes at low pressure, small hot water pipes and coils at high pressure, or hot air. The difference in working cost among these systems is much smaller than it is commonly supposed. We generally assume that in an open grate from 70 to 90 per cent of the heat generated escapes uselessly up the chimney. But the figures here given are not easily reconciled with

this view. Closed stoves are certainly more economical, as are also, in some cases, steam-pipes, but hot-water pipes are found in some towns more costly than open fires, though they are cheaper in others.

The working cost of heating is much influenced by the system of ventilation adopted, according as it is "natural" or "mechanical." In the former the foul air escapes by the chimney or by ventilators in the ceilings, whilst sewer-gas and ground-air are very liable to be drawn in with the entrance current. On the mechanical system, fresh air, admitted at inlets 12 to 15 feet from the ground and filtered through coarse jute cloth, is heated to the desired temperature and forced into the school-rooms by means of fans. From a sanitary point of view the mechanical system has a very decided advantage. In schools ventilated respectively on these two systems, if we take the temperature, the proportions of carbonic acid, of organic matter, and of micro-organisms in the air as 1 each, in a naturally ventilated school the temperature will be 0·66, the carbonic acid 1·7, the organic matter 7·0, and the micro-organisms 9·2. To get an equally pure atmosphere by opening windows and doors the rooms would be scourged with draughts, and during the greater part of the year they would be chilled to a dangerous degree.

The expense of the mechanical system is admittedly higher, but the perfection of the ventilation thus obtained would render school-rooms lower by one foot to two feet quite wholesome and pleasant. Thus, a very considerable economy would be effected in the building of schools. Dr. Carnelley decidedly recommends this system. His "Report" will be of great value to all persons concerned in the establishment and working of schools.

The Farmer's Guide to Manuring. By A. M. Pearson, Agricultural Chemist. Melbourne: R. S. Brain, Government Printer.

Some of the Agricultural Problems of Victoria. A Paper read before the Royal Commission on Vegetable Products. By A. M. Pearson (formerly of Bombay). Shepparton: Callandar and Co.

In the former of these pamphlets the author recognises the preponderating importance of Ville's four principles, nitrogen, phosphoric acid, potash, and lime. But he immediately adds that the farmer should simply buy the three former, as phosphoric acid is in general supplied in combination with lime. He recommends that the manures required on different soils and for different crops should be ascertained by trial plots.

In the treatise on the Agricultural Problems of Victoria he brings forward the same lesson, which is well worth putting in practice. Towards the conclusion he touches on a very important fault, not merely of the Australians, but of the British nation everywhere. They are too apt to content themselves with one or two staple products, agricultural or manufacturing, overlooking scores of minor industries which, if individually small, sum up to a mighty total. The Australian farmer makes a staple of wool, and the crops which he cultivates are generally the same as his fathers have been accustomed to grow in Britain with a yearly temperature lower by 10° F. and a very different rainfall. Mr. Pearson points out a number of products which India consumes largely, and which she imports at present to a large extent from alien countries situate at a much greater distance. Why, he asks, should not Australia supply India with wines, jams, dried fruit, olives and olive oil, pickles, &c.? He might have added that Australia should do a large export trade in silk, essential oils, cork, medicinal drugs, gums, and tanning matters. We may here remark that the cultivation of the *Pyrethrum roseum*, the plant from which "Persian Insect Powder" is made, has been successfully introduced in Victoria. We believe that the cultivation of such crops as those just enumerated must afford remunerative employment to five times as many persons as does sheep-farming. The author mentions the efficient preservation of butter and eggs for the Indian and British markets as a desideratum. Mr. Pearson's advice is most excellent. To develop the latent capabilities of all parts of the Empire and to bring them into increased connection with each other is a noble and a patriotic task.

CORRESPONDENCE.

A CHEMICAL PROBLEM.

To the Editor of the Chemical News.

Sir,—I have encountered in a sample of caustic potash, which was supplied to me as pure, a substance which has caused me an infinite amount of trouble and perplexity. The following are a few of the reactions given by this substance:—

(1). When the potash was fused with a quantity of potassium nitrate in a silver crucible, and the melt after the fusion was dissolved out by water, a peculiar looking liver-coloured matter, which collected into a spongy mass, remained undissolved, and the clear supernatant liquid, on being boiled, yielded a further small quantity of the same matter.

(2). This liver-coloured residue was easily soluble in HCl, in which it dissolved without evolution of gas.

(3). Water added to the HCl solution, even when the quantity of substance present was very minute, produced a white precipitate which was very well shown as an opalescent layer at the contact of the liquids, and which dissolved or remained permanent on shaking up the liquids according as the HCl or the H_2O was in excess. Heating also caused the precipitate to re-dissolve, even when the quantity of acid was very small. In the latter case it was re-produced as the liquid cooled.

(4). The compound dissolved in HCl could be precipitated by concentration as a white (faintly yellow—the HCl solution was amber coloured) subcrystalline salt, which dissolved in ammonium hydrate, but was immediately re-precipitated on expelling the ammonia by boiling as a white powder, which readily re-dissolved in ammonia or in HCl.

(5). The substance gave no decided bead colourations, but was (the crystals obtained by concentration from HCl solution) immediately reduced to a white, easily fusible bead in even a moderately reducing flame when placed in the flame in contact with a microsmic salt bead.

(6). Sulphuretted hydrogen in acid solutions gave a *dark brown* precipitate, almost exactly resembling the substance described in (1) in appearance.

(7). This sulphide was soluble in ammonium sulphide and also in strong hot HCl.

It is singular that the potash when H_2S was passed through it gave no precipitate (it darkened in colour), not even on adding HCl, till acid after the formation of a quantity of potassium sulphide. This makes it appear as though the action of the fused nitre had something to do with the conversion of the substance into the state in which it gives the above reactions.

I feel disposed to call this an elusive element whatever it is, and at any rate I suppose it must have eluded the manufacturer who supplies the potash as pure. I have tested it in innumerable ways, and I have had the assistance of a first class chemist, Mr. Barfoot, of Chesterfield, and at last I have been forced to conclude that the element present is a stranger.

It certainly is not antimony, bismuth, nor tin, nor is it tellurium, to which many of its reactions point, for it is not precipitated by sulphurous acid nor by a soluble sulphite under any circumstances, this test having been repeatedly tried with the utmost care.

I have collected a little of the substance and forwarded it to you in the form of sulphide, as I thought it might interest you.—I am, &c.,

R. SNOWDON.

Staveley Iron Works, Chesterfield, March 13, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 9, March 4, 1889.

Separation of Zinc and Cobalt.— H. Baubigny.—This memoir will be inserted in full.

Observations on Saccharification by Diastase.—L. Lindet.—The accumulation of maltose in worts arrests saccharification. When the maltose disappears in the state of alcohol and carbonic acid or of an insoluble phenylhydrazine compound the diastase resumes its saccharifying action upon the dextrine.

On the Phthalates; New Neutral and Acid Ethers of the Camphols.—A. Haller.—These ethers are formed under the same conditions as the succinates. The author has obtained the neutral and acid phthalates (dextro- and lævo-rotatory), and the neutral and acid racemic phthalates.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 2.

The Origin of Nitric and Nitrous Acid in Nature by the Evaporation of Water, by Alkaline Substances and by the Soil in itself.—Dr. Anton Baumann.—The author mentions that every kind of calcium carbonate, thoroughly washed in water to remove any existing nitrogen compounds, and dried at a high temperature, was found to contain nitrous acid. The same phenomenon was also observed in other substances, especially in those of a basic nature. Hence it was assumed that basic substances possess the property of converting ammonia, or even atmospheric nitrogen, into nitrogen oxides. This supposition was decidedly refuted by the result of the experiments. The phenomena observed are explained by the fact that in consequence of the combustion of the coal-gas used for heating the drying-stove nitrogen acids are formed and are absorbed by basic substances. The view of Franke that the soil, in virtue of the calcium carbonate which it contains, is able to convert ammonia into nitric acid is erroneous, and is founded on imperfect experiments. — *Land. Versuchsstationen.*

Detection of Nitrates in the Soil.—Prof. Kreusler.—Frank reports that the quartz grains of soil, even after repeated washing in water, are coloured blue with sulphuric acid containing diphenylamine, whence he inferred a peculiar surface reaction of the granules, by means of which they fix nitrates. Dr. Kreusler finds that certain oxides of iron and manganese give the same reaction. The brucine reaction is produced by the higher oxides of manganese just as it is by nitrates.—*Landwith. Jahrbucher.*

Studies and Investigations on the Humoid Compounds of Arable and Moor-land Soils.—C. G. Eggertz.—The author maintains that humic and ulmic acids do not naturally occur in peat and similar products, but are artificial laboratory products. The existence of the indifferent insoluble bodies, humine and ulmine, is very doubtful, whilst the soluble compounds, crenic and creno-hydrochloric acids, doubtless exist as independent bodies. He divides the products of decay existing in the soil into two classes—*mulloids*, which may be extracted by treatment with ammonia or potassa-lye, and *humoids*, which are obtained by acting upon the carbohydrates with mineral acids. He refutes the view of Mulder, that the nitrogen of the mull-substances is exclusively present as ammonium mullate.—*Neddelanden fran konigl. Landbruks-Akademiens Experimentalfält.*

Condition of Sulphur and Phosphorus in Plants, in the Soil, and in Humus.—MM. Berthelot and André.—From the *Comptes Rendus.*

The Peats of Alsace-Lorraine and their Value in Agriculture. — Dr. Barth. — The Alsacian peats of Dambach have a much less power of absorbing ammonia and alkalies than those of Holland and of Salm. The Lorraine peats of Bitsch and Ham are useful only as a material for composts.

Action of Artificial Manures upon White Mustard.—P. Budrin and Dr. Strecker (*Journal fur Landwithschaft*).—The yield of white mustard can be much increased by the use of nitrogenous manures—preferably sulphate of ammonia—either alone or along with phosphates. The effects of kainite do not appear favourable.

Adulteration of Linseed Meal.—Dr. E. Eidam.—The adulterant is the residue of castor-oil seeds, a poisonous purgative. The recognition of this fraud is effected by means of low microscope powers, when the characteristic longitudinal marbling of the castor seeds is detected.

The Chemical Action of Some Micro-organisms.—R. Warington.—From the *Journal of the Chemical Society.*

The Occurrence of Typhus Bacilli in Soils.—E. Mace.--From the *Comptes Rendus.*

Chemical Composition of Farmyard Manure.—F. Sestini (*Chem. Centralblatt*).—The author's results deviate in many cases widely from the accepted averages.

Adulteration of Bone-meal with Mineral Phosphates.—N. von Lorenz (*Oester. Ung. Zeitschrift fur Rubenzucker Industrie*).—The author's method turns on the recognition of fluorine in the mineral phosphates.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. iii., No. 33.

Utilisation of Sewage.—An account of the Berlin irrigation works. It is remarked that at least one hectare of irrigation ground is required to absorb and utilise the sewage of 250 persons, and the authorities hope to reduce the proportion to 200 persons. The land cannot be continuously treated with sewage, which would injure the crops and create sediments. Fields of cereals receive sewage only three or four times yearly, and not at all after the plant has germinated. Vegetables may be irrigated three or four times weekly.

Journal de Pharmacie et de Chemie. Vol. xix., No. 5.

New Proximate Principle in the Ergot of Rye.—Ergosterine, the principle in question, has been confounded with the cholesterine of animals. It has the composition $C_{52}H_{40}O_2,H_2O_2$. It crystallises from alcohol in nacreous tablets, and from ether in fine needles. It is quite insoluble in water and dissolves in 500 parts of cold alcohol at 96 per cent, and in 32 parts at the temperature of ebullition; in 45 parts of cold chloroform and in a few parts of the same liquid when hot. It melts at 154°, and boils in a vacuum at 185°. It is dextro-rotatory, and its specific gravity is 1·040. Ergosterine is slowly oxidised in contact with air, becoming coloured and odoriferous. It is not attacked by strong boiling alkaline

solutions. It is a monoatomic alcohol. If treated with nitric or hydrochloric acid and ferric chloride ergosterine gives the coloured reactions of cholesterine, but its reaction with sulphuric acid and chloroform is quite different. Strong sulphuric acid colours cholesterine brown and dissolves it incompletely, and agitation with chloroform extracts the greater part of the coloured product and turns orange-yellow, passing into red and violet on exposure to the air. Ergosterine, on the contrary, dissolves completely in the acid, and chloroform, if shaken up with the mixture, remains almost colourless.

The Sap of *Bassia latifolia*.—E. Heckel and Fr. Schlagdenhauffen.—The *Bassia latifolia* or Mohwa is a large sapotaceous tree, very common in India, and yields a small quantity of sap capable of furnishing gutta-percha, though only to the extent of 1·8 per cent.

Commercial Oleic Acid; its Falsification with Linoleic Acid; the Industrial Inconvenience of this Fraud and the Means for its Detection.—MM. Granval and Valser.—If the sophisticated oleic acid is used in spinning woollen yarns, no harm ensues if the yarns are woven at once; but if the yarns remain exposed for some weeks to air and light they assume a strong yellow colour, which cannot be removed. Besides, the the thread becomes rougher and glutinous, and occasions much waste and trouble in weaving. If we mix a few drops of the sophisticated oleic acid with an equal volume of soda-lye an intense yellow colour is produced, whilst pure oleic acid, if similarly treated, merely takes a grey colour. If we spread upon a plate of lead, previously scraped clean, a thin layer of oleic acid containing linoleic acid, and place for comparison a similar layer of pure oleic acid upon another plate of lead, the next morning the impure acid will be more or less completely resinified, whilst the pure acid is scarcely altered.

A New Reagent for Free Hydrochloric Acid in the Gastric Juice.—Dr. Boas.—The author prepares a solution containing, in 100 parts of dilute alcohol, 5 parts of resorcine and 3 parts of cane-sugar. Two or three drops of this reagent are added to five or six drops of gastric juice, and the mixture is heated in a porcelain capsule over a very small flame. After complete evaporation a rose-coloured or bright red coating is seen on the sides of the capsule if hydrochloric acid is present. If the heat is too strong the sugar is carbonised and the reaction may be masked. Albumenoid matters interfere by totally or partially neutralising the acid.—*Pharm. Zeitung.*

New Method of Determining Hydrochloric Acid in the Gastric Juice.— J. Sjögvist.—If gastric juice, mixed with barium carbonate, is evaporated to dryness the free acids are converted into barium salts. If the mixture is ignited the barium chloride undergoes no change, whilst the barium salts of the organic acids are re-converted into carbonate. The ash is exhausted with water, the chloride is dissolved out, and the barium in solution is determined volumetrically with potassium bichromate in presence of acetic acid. Tetramethylparaphenylenediamine paper may be used as an indicator.—*Zeitschrift für Physiologische Chemie.*

MISCELLANEOUS.

Treatise on Manures. — Dr. A. B. Griffiths's "Treatise on Manures" will be published in a few days by Messrs. Whittaker and Co., of Paternoster Square.

The Chemical Laboratory of Wiesbaden.—In the winter term 1888 to 1889 there were 58 students on the books. Of these, 38 were from Germany, 5 from England, 4 from North America, 3 from Sweden, 3 from Russia, 2 from Spain, 1 from Holland, 1 from France, and 1 from Italy. Besides the directors, Geh. Hofrath Prof. R. Fresenius, there are engaged as teachers Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. F. Hueppe, and Architect F. Brahm. The assistants in the Instruction Laboratory are 2 in number, in the Private Laboratory 15, and in the Versuchstation 3. Besides the scientific researches a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchstation on behalf of manufacture, trade, mining agriculture, and hygiene.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Iron Oxide Paint.—The ingredients can probably be obtained from Herring's, 40, Aldersgate Street, E.C.—G. A. Keyworth, Hastings.

Iron Oxide Paint.—Noticing in your last issue a query as to where the raw material for iron oxide paint can be obtained, we beg to inform you that we are makers of a pure quality of levigated iron oxide testing over 94 per cent iron, calculated as Fe_2O_3. This is ready for use by paint-makers, requiring only the addition of boiled oil.—Brooke, Simpson, and Spiller (Limited).

White Glaze for Bricks, &c.—I shall feel obliged if any reader of the Chemical News will advise me what book to get which will give me reliable information on this subject. I am acquainted with the manufacture and use of coloured glazes; but the white glazes I have tried have unequal expansion and contraction with the body of the brick, and in consequence crack in fine network fissures.—A Potter.

MEETINGS FOR THE WEEK

Monday, 25th.—Medical, 8.30.
— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.

Tuesday, 26th.—Institute of Civil Engineers, 8.
— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
— Royal Medical and Chirurgical, 8.30.
— Sanitary Institute, 8. "Sanitary Appliances," by Prof. W. H. Corfield.
— Society of Arts, 8. "Borneo," by Robert Pritchett

Wednesday, 27th.—Society of Arts, 8. "Objects and Methods of the Society of Arts' Motor Trials," by Prof. A. B. W. Kennedy, F.R.S. (Adjourned Discussion).

Thursday, 28th.—Royal, 4.30.
— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
— Institute of Electrical Engineers, 8.
— Chemical, 8. (Anniversary Meeting). Address by the President on "Recent Researches on the Rare Earths as Interpreted by the Spectroscope." Election of Office Bearers and Council

Friday, 29th.—Royal Institution, 9. "Yeast," by A. Gordon Salamon, F.C.S.
— Society of Arts, 8. "The Progress of the Railways and Trade of India," by Sir Juland Danvers.
— Sanitary Institute, 8. "Food (including Milk), Sale of Food and Drugs Act," by C. E. Cassal, F.C.S.

Saturday, 30th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. / Stöchiometry .. .. / Organic Chemistry .. .. / Chemical Technology .. .. — W. FRESENIUS, Ph.D.
Microscopy, with exercises in Microscopic work .. .. — E. BORGMANN, Ph.D.
Chemistry and Analysis of Foods .. — Prof. H. FRESENIUS, Ph.D. / E. BORGMANN, Ph.D. / W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene .. .. / Practical exercises in Bacteriology .. — Dr. med. F. HUEPPE.
Technical Drawing, with exercises .. — F. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1531.

ON THE COMPOSITION OF WATER.*

By Lord RAYLEIGH, Sec.R.S.

During the past year I have continued the work described in a former communication on the relative densities of hydrogen and oxygen,† in the hope of being able to prepare lighter hydrogen than was then found possible. To this end various modifications have been made in the generating apparatus. Hydrogen has been prepared from potash in place of acid. In one set of experiments the gas was liberated by aluminium. In this case the generator consisted of a large closed tube sealed to the remainder of the apparatus; and the aluminium was attached to an iron armature so arranged that by means of an external electro-magnet it was possible to lower it into the potash or remove it therefrom. The liberated gas passed through tubes containing liquid potash,‡ corrosive sublimate, finely powdered solid potash, and, lastly, a long length of phosphoric anhydride. But the result was disappointing, for the hydrogen proved to be no lighter than that formerly obtained from sulphuric acid.

I have also tried to purify hydrogen yet further by absorption in palladium. In his recent important memoir,§ "On the Combustion of Weighed Quantities of Hydrogen and the Atomic Weight of Oxygen," Mr. Keiser describes experiments from which it appears that palladium will not occlude nitrogen—a very probable impurity in even the most carefully prepared gas. My palladium was placed in a tube sealed, as a lateral attachment, to the middle of that containing the phosphoric anhydride, so that the hydrogen was submitted in a thorough manner to this reagent both before and after absorption by the palladium. Any impurity that might be rejected by the palladium was washed out of the tube by a current of hydrogen before the gas was collected for weighing. But as the result of even this treatment I have no improvement to report, the density of the gas being almost exactly as before.

Hitherto the observations have related merely to the densities of hydrogen and oxygen, giving the ratio 15·884, as formerly explained. To infer the composition of water by weight, this number had to be combined with that found by Mr. Scott as representing the ratio of volumes. The result was—

$$\frac{2 \times 15{\cdot}884}{1{\cdot}9965} = 15{\cdot}914.$$

The experiments now to be described are an attempt at an entirely independent determination of the relative weights by actual combustion of weighed quantities of the two gases. It will be remembered that in Dumas's investigation the composition of water is inferred from the weights of the oxygen and of the water, the hydrogen being unweighed. In order to avoid the very unfavourable conditions of this method recent workers have made it a point to weigh the hydrogen, whether in the gaseous state, as in the experiments of Professor Cooke and my own, or occluded in palladium, as in Mr. Keiser's practice. So long as the hydrogen is weighed, it is not very material whether the second weighing relate to the water or to the oxygen. The former is the case in the work of Cooke and Keiser, the latter in the preliminary experiments now to be reported.

Nothing could be simpler in principle than the method adopted. Globes of the same size as those employed for the density determinations are filled to atmospheric pressure with the two gases, and are then carefully weighed. By means of Sprengel pumps the gases are exhausted into a mixing chamber, sealed below with mercury, and thence, by means of a third Sprengel, are conducted into a eudiometer, also sealed below with mercury, where they are fired by electric sparks in the usual way. After sufficient quantities of the gases have been withdrawn, the taps of the globes are turned, the leading tubes and mixing chamber are cleared of all remaining gas, and, after a final explosion in the eudiometer, the nature and amount of the residual gas are determined. The quantities taken from the globes can be found from the weights before and after operations. From the quantity of that gas which proved to be in excess the calculated weight of the residue is subtracted. This gives the weight of the two gases which actually took part in the combustion.

In practice, the operation is more difficult than might be supposed from the above description. The efficient capacity of the eudiometer being necessarily somewhat limited, the gases must be fed in throughout in very nearly the equivalent proportions; otherwise there would soon be such an accumulation of residue that no further progress could be made. For this reason nothing could be done until the intermediate mixing chamber was provided. In starting a combustion this vessel, originally full of mercury, was charged with equivalent quantities of the two gases. The oxygen was first admitted until the level of the mercury had dropped to a certain mark, and subsequently the hydrogen down to a second mark, whose position relatively to the first was determined by preliminary measurements of volume. The mixed gases might then be drawn off into the eudiometer until exhausted, after which the chamber might be re-charged as before. But a good deal of time may be saved by replenishing the chamber from the globes simultaneously with the exhaustion into the eudiometer. In order to do this without losing the proper proportion, simple mercury manometers were provided for indicating the pressures of the gases at any time remaining in the globes. But even with this assistance close attention was necessary to obviate an accumulation of residual gas in the eudiometer, such as would endanger the success of the experiment, or, at least, entail tedious delay. To obtain a reasonable control, two sparking places were provided, of which the upper was situate nearly at the top of the eudiometer. This was employed at the close, and whenever in the course of the combustion the residual gas chanced to be much reduced in quantity; but, as a rule, the explosions were made from the lower sparking point. The most convenient state of things was attained when the tube contained excess of oxygen down to a point somewhat below the lower sparking wires. Under these circumstances each bubble of explosive gas readily found its way to the sparks, and there was no tendency to a dangerous accumulation of mixed gas before an explosion took place. When the gas in excess was hydrogen the manipulation was more difficult, on account of the greater density of the explosive gas retarding its travel to the necessary height.

In spite of all precautions several attempted determinations have failed from various causes, such as fracture of the eudiometer and others which it is not necessary here to particularise, leading to the loss of much labour. Five results only can at present be reported, and are as follows:—

December	24, 1888	.. ..	15·93
January	3, 1889	.. ..	15·98
,,	21, ,,	.. ..	15·98
February	2, ,,	.. ..	15·93
,,	13, ,,	.. ..	15·92
	Mean	.. ..	15·95

* A Paper read before the Royal Society, March 7, 1889.

† *Roy. Soc. Proc.*, February, 1888 (vol. xliii., p. 356).

‡ Of course this tube was superfluous in the present case, but it was more convenient to retain it.

§ *Am. Chem. Jour.*, vol. x, No. 4.

This number represents the atomic ratio of oxygen and hydrogen as deduced immediately from the weighings with allowance for the unburnt residue. It is subject to the correction for buoyancy rendered necessary by the shrinkage of the external volume of the globes when internally exhausted, as explained in my former communication.* In these experiments the globe which contained the hydrogen was the same (14) as that employed for the density determinations. The necessary correction is thus four parts in a thousand, reducing the final number for the atomic weight of oxygen to—

15·89,

somewhat lower than that which I formerly obtained (15·91) by the use of Mr. Scott's value of the volume ratio. It may be convenient to recall that the corresponding number obtained by Cooke and Richards (corrected for shrinkage) is 15·87, while that of Keiser is 15·95.

In the present incomplete state of the investigation, I do not wish to lay much stress upon the above number, more especially as the agreement of the several results is not so good as it should be. The principal source of error of a non-chemical character is in the estimation of the weight of the hydrogen. Although this part of the work cannot be conducted under quite such favourable conditions as in the case of a density determination, the error in the difference of the two weighings should not exceed 0·0002 grm. The whole weight of the hydrogen used is about 0·1 grm.;† so that the error should not exceed three in the last figure of the final number. It is thus scarcely possible to explain the variations among the five numbers as due merely to errors of the weighings.

The following are the details of the determination of February 2, chosen at random :—

Before combustion—

$G_{14}+H+0·2906=G_{11}$ pointer 20·05

After combustion—

$G_{14}+H+0·4006=G_{11}$ pointer 20·31

Hydrogen taken = 0·1100 − 0·00005 = 0·10995 grm.

Before combustion—

$G_{13}+O=G_{11}+2·237$ pointer 20·00

After combustion—

$G_{13}+O=G_{11}+1·357$ pointer 19·3

Oxygen taken = 0·8800 + 0·0001 = 0·8801 grm.

At the close of operations the residue in the eudiometer was oxygen, occupying 7·8 c.c. This was at a total pressure of of 29·6 − 16·2 = 13·4 inches of mercury. Subtracting 0·4 inch for the pressure of the water vapour, we get 13·0 as representing the oxygen pressure. The temperature was about 12° C. Thus, taking the weight of a c.c. of oxygen at 0° C., and under a pressure of 76·0 c.m. of mercury to be 0·00143 grm., we get, as the weight of the residual oxygen—

$$0·00143\frac{7·8}{1+12\times 0·00367}\frac{13·0\times 2·54}{76·0}=0·0046 \text{ grm.}$$

The weight of oxygen burnt was, therefore,—

0·8801 − 0·0046 = 0·8755 grm.

Finally, for the ratio of atomic weights—

$$\frac{\text{Oxygen}}{\frac{1}{4}\text{ Hydrogen}}=15·926$$

In several cases the residual gas was subjected to analysis. Thus, after the determination of February 2, the volume was reduced by additions of hydrogen to 1·2 c.c. On introduction of potash there was shrinkage to about 0·9, and, on addition of pyrogallic acid, to 0·1 or 0·2. These volumes of gas are here measured at a pressure of ¼ atmosphere, and are, therefore, to be divided by 3 if we wish to estimate the quantities of gas under standard conditions. The final residue of (say) 0·05 c.c. should be nitrogen, and, even if originally mixed with the hydrogen—the most unfavourable case—would involve an error of only 1-2000th in the final result. The 0·1 c.c. of carbonic anhydride, if originally contained in the hydrogen, would be more important; but this is very improbable. If originally mixed with the oxygen, or due to leakage through indiarubber into the combustion apparatus, it would lead to no appreciable error.

The aggregate impurity of 0·15, here indicated, is tolerably satisfactory in comparison with the total quantity of gas dealt with — 2000 c.c. It is possible, however, that nitrogen might be oxidised, and thus not manifest itself under the above tests. In another experiment the water of combustion was examined for acidity, but without definite indications of nitric acid. The slight reddening observed appeared to be rather that due to carbonic acid, some of which, it must be remembered, would be dissolved in the water. These and other matters demand further attention.

The somewhat complicated glass blowing required for the combustion apparatus has all been done at home by my assistant, Mr. Gordon, on whom has also fallen most of the rather tedious work connected with the evacuation of globes and other apparatus, and with the preparation of the gases.

A METHOD OF EXAMINING RATE OF CHEMICAL CHANGE IN AQUEOUS SOLUTIONS.*

By G. GORE, LL.D., F.R.S.

THIS research supplies an outline of a method of examining chemical change, based upon the application of the "voltaic balance" to measuring the relative amounts of voltaic energy of electrolytes (see *Roy. Soc. Proc.*, vol. xliv., pp. 151, 294; *Ibid.*, vol. xlv., p. 268), and the rate of chemical change is indicated by alterations in amount of such energy.

The author gives an example of two liquids, viz., a solution of equivalent proportions of potassic iodide and chlorine, and one of chloride of potassium and iodine, which, although having the same ultimate chemical composition, are greatly different, viz., as 31·76 to 1·0, in amount of voltaic energy.

The results of the experiments show that the solution of potassic iodide and chlorine was very unstable, highly sensitive to rise of temperature, had a great tendency to lose its voltaic energy, to change its chemical composition, and approach that of the other mixture. That the solution of the latter was very much more stable and much less sensitive to heat, but had a feeble tendency to absorb energy, to change its chemical composition, and approach that of the solution of potassic iodide and chlorine. The effect, therefore, of heating both liquids was to produce two portions possessing similar chemical composition and properties, consisting of about 0·23 part of potassic iodide, 74·49 of potassic chloride, 126·8 of iodine, and 0·0497 of chlorine. They also show that the solution of potassic iodide and chlorine decomposes spontaneously at 12° C. into potassic chloride and free iodine; that more than six days are necessary to effect the complete chemical change at that temperature; and that the rate of chemical

* The necessity of this correction was recognised at an early stage, and, if I remember rightly, was one of the reasons which led me to think that a re-determination of the density of hydrogen was desirable. In the meantime, however, the question was discussed by Agamennone ("Atti (Rendiconti) d. R. Acad. dei Lincei," 1885), and some notice of his work reached me. When writing my paper last year I could not recall the circumstances; but since the matter has attracted attention I have made inquiry, and take this opportunity of pointing out that the credit of first publication is due to Agamennone.

† It was usual to take for combustion from two-thirds to three-fourths of the contents of the globe.

* Abstract of a Paper read before the Royal Society, March 14, 1889.

change is much greater at the commencement of the action than towards its termination.

The collective results show that the "voltaic balance" method may be used to detect chemical changes of aqueous solutions and to measure their rate. Its great advantage over the colorimetric method is that it is equally applicable to colourless liquids; it is much more sensitive and exact usually than either the colorimetric or the thermo-chemical method, and it is quick and easy of performance. It is being used to detect and measure chemical changes produced by light in aqueous solutions. The degree of freedom of an aqueous solution of chlorine from hydrochloric acid and of iodine from hydriodic acid was ascertained much more readily by this method than by ordinary chemical analysis.

ON THE SEPARATION OF ZINC AND COBALT.

By H. BAUBIGNY.

The author has already shown how accurately zinc and nickel can be separated in an acid solution by means of sulphuretted hydrogen. He has also shown that in a distinctly acid solution the salts of cobalt are less easily transformed into sulphide than those of nickel, whence there was room to think that the method which had succeeded with nickel might be equally applicable to cobalt in presence of zinc. Experiment, however, showed that it is often defective. The process is accurate only if we have little cobalt in proportion to the zinc, 5 to 6 per cent at the most. Otherwise the precipitate of zinc contains cobalt and takes a watery green colour, due to the existence of a compound of the two sulphides of zinc and cobalt, which is, among sulphides, analogous to Rinman's green among the oxides. For if we mix weights of the sulphides of zinc and cobalt equal to those contained in the precipitate formed in the zinco-cobaltic liquid we have a blackish grey product. This green sulphide may in some cases contain as much as three or four per cent of its weight of cobalt sulphide.

If we operate as in the case of nickel, and even raise the percentage of acetic acid in the solution for a synthetic mixture of 0·249 grm. $ZnSO_4$ and 0·250 grm. $CoSO_4$, the green sulphide formed, and filtered after standing an hour at 16° gave 0·256 grm. of rose-coloured $ZnSO_4$, which, when treated anew by the same method, was resolved into 0·249 grm. $ZnSO_4$ and 0·007 $CoSO_4$.

If the proportion of zinc is notably increased, the weight of the cobalt sulphide precipitated with that of zinc increases, and in this case the sulphide turns black in less than an hour. This takes place with a mixture of 0·037 grm. $ZnSO_4$ and 0·4625 grm. $CoSO_4$ in an acetic solution of 25 per cent. After standing for sixteen hours the weight of the CoS formed was 0·130 grm. $CoSO_4$, or about 30 per cent of the cobalt taken for the experiment.

The action, therefore, varies with the nature of the elements, nickel or cobalt, placed in presence of zinc even under conditions where sulphuretted hydrogen alone acts neither on the salts of nickel nor those of cobolt—a fact not unprecedented in the history of the sulphides.

In any case the comparison of the two last experiments leads us to conclude that zinc sulphide, even in small quantities, is capable of provoking the decomposition of cobalt sulphate in the cold, in presence of sulphuretted hydrogen, and in a strongly acetic solution if there is not at the beginning of the experiment a decided quantity of free sulphuric acid. The author then sought to solve the problem of the separation of cobalt and zinc by taking as free acid sulphuric acid, suitably diluted, so as not to hinder the total precipitation of the zinc, confining himself, however, to the case where the weight of the free acid is about equal to that of the acid existing in combination in the salts present. Under such conditions, and letting the sulphide formed settle for three hours at 16° the following results were obtained:—

Mixture in 400 *c.c.*

	Taken.	Found.
$ZnSO_4$	0·055 grm.	0·055 grm.
$CoSO_4$	0·468 „	0·4685 „
SO_3 (free)	0·262	

If the weights found are satisfactory the cobalt sulphide had still a very faint green tint and the zinc sulphide a rose. These colours were due to slight traces of cobalt of about the tenth of a milligrm., so that the separation is evidently not absolute. Experiment shows that in the case of a mixture of the same total weight—about half a grm.—if the quantities of the two metals are less unequal the deviation between the weight of the salts taken and those found may extend to 2 m.grms. (in excess for zinc sulphate and in deficiency for cobalt) and increases in larger weights.

The green tint which zinc sulphide takes if formed in presence of considerable quantities of salts of cobalt has never been previously mentioned; still it may be observed on using citric and oxalic acids, which have been recommended by various authorities in reliance upon the different action of sulphuretted hydrogen upon the corresponding salts of zinc and cobalt in solutions acidulated with an excess of the same acid. This fact is not surprising, since sulphuric and nitric acids leave the chemist to encounter the same difficulties.

Cobalt and zinc, even as sulphates, cannot be accurately separated by sulphuretted hydrogen in presence of a small excess of free sulphuric acid, except the quantity of cobalt is relatively small. The separation is still sufficiently approximate if there is, on the other hand, very little zinc. But, except under these restrictions, the best method for obtaining a correct determination is to reconvert the zinc precipitate into sulphate, and submit it to a second determination. The author will subsequently give the conditions for separating zinc from nickel and cobalt by the dry way. It depends on the absolute fixity of nickel and cobalt chlorides at the boiling-heat of sulphur, whilst, at the same heat, zinc chloride has a considerable vapour-tension.—*Comptes Rendus* (vol. cviii., p. 450).

ON THE TRUE FORMULA FOR PERMANGANATES.*

By CHARLES M. BRADBURY, of Virginia.

(Concluded from p. 138).

(1).

The Specific Heats of Potassium Permanganate and Potassium Perchlorate.

According to the law of Dulong and Petit, the specific heats of elements in the solid state vary inversely as their atomic weights. In the present state of chemistry this law is received with reservations, yet a high degree of probability attaches to deductions from it.†

Although the fact established by Kopp,‡ that the molecular heats of compounds are the sums of the atomic heats of their constituent elements, cannot be directly applied to fixing molecular weights by means of specific heats; yet it has been observed, in connection with the specific heats of solid compounds, that there is in general an inverse variation between their specific heats and

* Dissertation presented to the Faculty of the University of Virginia in application for the degree of Doctor of Philosophy. *Thesis*:—Permanganic acid is monobasic, and the permanganates are represented by the general formula $R(MnO_4)n$.

† R. and S., II., i., 16.

‡ R. and S., II., i., 20.

molecular weights, similar to that established by Dulong and Petit for the solid elements, *where the substances compared are of analogous composition.** Without assuming any closer analogy between permanganates and perchlorates than is actually revealed by analysis (thus leaving the question of the molecular weight of the former open), it would seem fair to expect from them conformity to this rule; for the only difference that analysis shows is the replacement of manganese in the one salt by chlorine in the other.†

It follows, then, that if the specific heats of potassium perchlorate and potassium permanganate as determined by experiment are nearly alike, their molecular weights will also be similar. According to Kopp,‡ the specific heat of potassium permanganate is 0·179; that of potassium perchlorate, 0·190. The molecular weight of $KClO_4$ is 138·25; that of potassium permanganate should, then, be somewhere near ($138{\cdot}25 \times \frac{179}{190} =$) 147+. But the formula $K_2Mn_2O_8$ requires a molecular weight of 314·42. By taking the formula $KMnO_4$ with half of this molecular weight there is an evident agreement (even though it be not very close) between the molecular weight as usually calculated, and as indicated by specific heat, *i.e.*, 157·21 and 147 + respectively.

(2).

The Specific Volume Relations.

The isomorphism of perchlorates with permanganates was announced by Mitscherlich,§ who made comparative measurements of the two classes of crystals. His results have been very generally received and confirmed by subsequent investigators.

According to the general law that *isomorphous compounds have equal specific volumes, while those whose crystal forms are approximately the same have also approximately equal specific volumes*,‖ the specific volumes of potassium perchlorate and potassium permanganates must be very nearly the same. But if $K_2Mn_2O_8$ be the correct formula for the permanganate, this is not the case; for the specific gravity of potassium permanganate is 2·644,¶ giving a specific volume (with this formula) of ($314{\cdot}42/2{\cdot}644 =$) 118·9; whilst the specific gravity of the perchlorate is 2·47,¶ which gives a specific volume of ($138{\cdot}25/2{\cdot}47 =$) 55·9. It is evident that this wide difference disappears when the formula $KMnO_4$ is substituted for $K_2Mn_2O_8$. The specific volume of potassium permanganate then becomes 59·4, which is not far from 55·9.

(3).

The General Chemical Relation of Isomorphous Bodies.

The relation referred to is thus concisely expressed by Richter:** "From the isomorphism of two compounds may be concluded an analogous chemical composition, a similar number of atoms in the molecule." This statement is qualified in its context as accuracy requires. With all necessary limitations, it yet adds something to the evidence which, as a whole, points so unmistakably to the monobasic character of permanganic acid and the heptad valence of the manganese in it. Potassium permanganate must, like potassium perchlorate, contain six and not twelve atoms in its molecule.

This paragraph, of course, is practically the same as the preceding, but presents the argument in more general form. As both are dependent on the isomorphism of the two salts compared, it should be noted that it is not essential to their validity that this isomorphism should be perfect, which is probably not the case. No investigator has been found, however, to deny at least a general isomorphism between the two classes of salts. Mitscherlich stated that the primitive form of both permanganate and perchlorate of potash is the right rhombic prism,* and this was afterwards alluded to by Gmelin, curiously enough, as an exception to the recognised rule that isomorphism argues chemical similarity, on the ground that "manganese bears no relation to chlorine."† That manganese does bear relations to chlorine is, as has been remarked, an unavoidable inference from the periodic system.

SUMMARY AND CONCLUSION.

It appears from the foregoing that there has not been, and is not now, any tangible proof in the shape of double salts to show that permanganic acid is dibasic; but that unless manganese be regarded as heptad in this acid, the monobasic formula is abnormal. But it is tolerably clear that manganese may be so regarded, notwithstanding its artiad character in most of its compounds; and it follows that the monobasic formula does not violate any law of chemistry, and being the simpler of the two should, according to the law of parcimony, be given precedence of the dibasic for this reason alone. In addition to this, however, it has been shown that the relations of permanganic acid to another acid known to be monobasic point conclusively to the monobasic formula as the only correct one; the relations, namely, between its potassium salt and that of perchloric acid with regard to (1) specific heat, (2) specific volume, and (3) crystal form.

The above arguments are not offered as a rigid demonstration of the thesis. The intrinsic difficulties of the subject are such as well nigh forbid an unanswerable course of reasoning, since the evidence is to a large extent merely negative in character. Nevertheless, the accumulated weight of the facts adduced in favour of the thesis—the facts of experiment, of authority, and of chemical law—are such as give to it a degree of probability that is only short of actual certainty.

ADDENDUM.

Dr. Auwers, of Göttingen, has recently given special attention to Raoult's method of determining molecular weights by observing the freezing-points of solutions. His published results have been obtained from organic substances, and with other solvents than water; and although M. Raoult himself seems to have determined "depression-coefficients" for various inorganic substances, I have not been able to find any detailed account of his work. It seemed worth while, therefore, to make an examination, even though a very brief one (as it necessarily was, owing to pressure of other work), of the relations between the freezing-points of solutions of substances whose molecular weights are well known, and of potassium permanganate.

Seven salts of potassium were examined—K_2SO_4, $KHCO_3$, K_2CrO_4, KNO_3, $KClO_3$, KIO_3, and $KClO_4$. In each case an accurately weighed portion (either one or two grms.) was dissolved in 100 molecules of water, or at the least multiple of 100 molecules that would dissolve it readily, and the solution was then frozen, the temperature of solidification being carefully noted. Where 200, 300, &c., molecules of water were used instead of 100, the observed depressions were multiplied by 2, 3, &c., respectively, since, other things being equal, the depression varies inversely as the amount of the solvent. The values thus found were as follows:—

	A.
1. K_2SO_4	2·38
2. $KHCO_3$	1·86
3. K_2CrO_4	2·60
4. KNO_3	1·65
5. $KClO_3$	1·73
6. KIO_3	2·00
7. $KClO_4$	1·80
Average value of T ..	2·00

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* "Watts' Dict.," iv., 36.
† Cf. Mitscherlich, *Ann. Chem. Phar.*, ii., 10; Serullas, *Ann. Chim. Phys.* (2), xlvi., 303; Mitscherlich, *Ann. Chim. Phys.*, xlix., 113.
‡ "Watts' Dict.," 1st Supp., 667.
§ *Ann. Chim. Phys.* (2), xlix., 129.
‖ "Fownes' Chem.," 232. Also "Watts' Dict."
¶ See "Notes on Work" (1), infra.
** "Inorganic Chemistry," 251.

* *Ann. Chem. Pharm.*, ii., 9.
† "Handb. of Chem.," i., 88.

If we reject the first three salts from consideration, on the ground that they are dibasic and not analogous to the others, the average value of T becomes 1·80.

Three separate solutions of potassium permanganate were made, of uniform strength, *i.e.*, 2 grms. of permanganate in 136·7 c.c. of water, or 600 molecules of water to 1 molecule of permanganate, supposing the permanganate to be $KMnO_4$. The solutions were frozen, and the *observed* depressions of the freezing-point below 0° C. were 0·33°, 0·32°, and 0·35°, an average of 0·33⅓°.

Supposing the true formula of the salt to be $K_2Mn_2O_8$, it is evident that the amount of water used was not really 600 molecules to one of the permanganate, but 1200, since on this hypothesis the same weight of the salt would have only half the number of molecules. Hence the observed depression, 0·33⅓°, must be regarded as $\frac{1}{7\frac{1}{2}}$ of T, and T = 4·00.

Such a value of T is altogether in excess of any other value found, even for the salts known to be dibasic.

If, however, $KMnO_4$ be the correct formula, T becomes 2·00, which is exactly the average value for all the salts examined, and is not much greater than the average value (1·80) for the monobasic salts.

Hence, $KMnO_4$ is the true formula, and permanganic acid is monobasic.

Notes on Work.

(1). *The Specific Gravities of Potassium Permanganate and Potassium Perchlorate.*

In selecting a liquid in which to take these specific gravities, the use of water being impossible, it was, of course, necessary not only that it should not dissolve the permanganate, but that it should be free from reducing action on that very easily decomposable salt. Refined petroleum was found to answer the purpose admirably. The liquid used was an illuminating oil of the best grade known as "Pratt's Astral Oil." Its sp. gr. at 20° C. was found to be 0·793. The crystals of permanganate were crushed to a rather coarse powder; 1·24 grms. were put into a miniature flask of about 25 m.m. diameter with long, gradually tapering neck, then covered with the oil, and gently agitated till free from air bubbles. The flask was next immersed in a bath of water at about 18° C.; it was roughly filled with oil at that temperature from another vessel already in the bath, and the whole was raised to exactly 20°. The liquid in the neck of the flask was carefully brought to the level of the mark with a very fine pipette. The flask was then removed, wiped dry, set in the balance-case for a quarter of an hour, and weighed. Similar precautions were observed in all of the filling and weighings.

The sp. gr. of the permanganate relative to the oil was found to be 3·334: which reduced to the standard of distilled water at 20° C., gives 2·644.

The sp. gr. of the perchlorate was taken in the same way. It was found to be 2·470.

(2). *The Preparation of Barium Permanganate.*

The manufacture of barium manganate, preparatory to converting it into permanganate, was found to be hardly so simple a matter as might be inferred from the language of many of the books. It is necessary to have the materials present in as nearly the right proportion as may be, a large excess of manganese dioxide preventing the formation of the manganate. The temperature must be properly regulated, otherwise no manganate is formed or, on the other hand, it is decomposed by excessive heat. Lastly, the reaction is very sensibly aided by blowing air into the crucible. This is in accordance with the observation of Desclabissac ("Watts' Dictionary," vii., 771), that contact of air is essential to the formation of good oxidation products, oxidising salts alone not being sufficient.

After several attempts with unsatisfactory results (including exposure of the material in a shallow tray in the muffle) nitrate of barium and manganese dioxide were taken in proportion of their molecular weights, the reaction—

$$Ba(NO_3)_2 + MnO_2 = BaMnO_4 + 2NO_2$$

—being assumed. That is, three parts of barium nitrate and one of manganese dioxide were finely pulverised, intimately mixed and placed in a No. 10 Beaufay crucible. The crucible was loosely covered with an iron sand-bath, through the middle of which was introduced an iron pipe reaching to the bottom of the crucible and connected with a small foot-bellows. The crucible was then placed in the wind-furnace and heated to bright redness, a current of air (sufficiently gentle to avoid blowing out the loose powder) being meanwhile kept up. The contents of the crucible now became liquid, and the air was briskly bubbled through. In a few minutes the mass stiffened. The current of air and the bright red heat were continued, however, for about three-quarters of an hour longer, at the end of which time a homogeneous mass of brilliant green manganate was found. Another charge, during the fusion of which the air-pipe became stopped, was duller in colour and not homogeneous. The same was true of a previous charge in which the air-blast was not used.

The manganate was pulverised and converted into permanganate with carbon dioxide, as usual.

(3). *Attempt to Prepare Sodium Manganate.*

It is stated in "Watts's Dictionary (iii., 818) on the authority of Gentele, that manganate of soda is produced when equal parts of finely pulverised manganese dioxide and sodium nitrate are heated to bright redness, in a muffle, for sixteen hours. Wöhler, however, is quoted as denying that any manganate can be formed in this way, for the reason that "the nitrate is entirely decomposed before the temperature is attained at which it can act on the manganese dioxide," and (we must infer) the remaining caustic soda, unlike caustic potash under similar circumstances, does not act on the manganese dioxide.

I followed the directions of Gentele with care, using a tray of Russia iron to hold the mixture of the two salts; but the result was entirely in accordance with Wöhler's statement. Within a half-hour after introducing the tray into the muffle, nearly all visible action had ceased; and after the sixteen hours of heating to bright redness had passed, the tray contained nothing but manganese dioxide and caustic soda.

It seemed possible that by heating the MnO_2 to redness and throwing into the fused nitrate, combination might be brought about. The attempt was made with the aid of the air-blast and wind-furnace used in the preparation of the barium salt, but even thus no manganate was formed. Lack of time forbade further experiments at the furnace, and the sodium permanganate wanted was easily made by mixing solutions of barium permanganate and sodium sulphate.

(4). *The Solubility of Potassium Permanganate.*

Not finding an extended statement of this solubility in any work to which I had access, I undertook to determine it.

A flat porcelain dish, about 6 c.m. deep and 25 in diameter, was covered outside with cotton-wool and heavy paper, and fitted with a wooden cover. The salt was placed in a small beaker, in sufficient quantity to ensure saturation of the solution, and the beaker was immersed in the bath in the dish through an opening made in the cover to fit it. The temperature of the bath was shown by a thermometer, introduced through the cover, and that of the solution by another suspended in it.

Starting at 0° C., the temperature was gradually raised by removing the ice and adding warm water, till thirty degrees was reached; from which point the increase was continued by the aid of a jet of steam led through the cover into the bath. At every five degrees rise in the temperature of the solution, 5 c.c. were removed to a weighed vial, which was then set in a steam-bath to

evaporate. The solution was stirred, and then given time for the undissolved salt to subside, previous to the removal of each sample. The practical difficulties in getting trustworthy results increased with the temperature. The pipette was kept hot by suspension in a flask over boiling water, and rinsed with hot water each time it was used to avoid the otherwise inevitable accumulation of solid salt in it.

The following figures show the average of three determinations. From 0° to 30° the results of the three determinations were practically identical, 0° and 5° absolutely so. From 35° up there were occasional rather wide disagreements among the results, making the increase in the average less regular. T shows temperature, and W the weight of solid salt contained in 100 c.c. of a saturated solution at that temperature.

T.	W. (Grms).	T.	W.	T.	W.	T.	W.
0	3·0	25	7·0	50	13·7	75	22·8
5	3·3	30	8·2	55	15·6	80	24·8
10	4·0	35	9·7	60	16·7	85	26·6
15	4·9	40	10·6	65	19·2	90	28·6
20	5·8	45	13·1	70	22·2	95	32·8

The approximate solubility often given of 1 in 16 at 15°, agrees more nearly with that at 20° in the above.

(5). *Solubility of Potassium Perchlorate.*

This was found by the same method as the preceding; the results given are the mean of the two most reliable determinations.

T.	W. (Grms).	T.	W.	T.	W.	T.	W.
0	0·7	25	1·6	50	4·0	75	9·5
5	0·8	30	2·0	55	5·2	80	9·1
10	1·0	35	2·6	60	6·1	85	11·1
15	1·1	40	3·0	65	7·4	90	13·4
20	1·3	45	3·7	70	8·2	95	13·2

The apparent interchange between 75° and 80°, and 90° and 95° shows the results as actually obtained and confirmed by repeated determinations.

OFFICIAL METHODS OF ANALYSIS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR 1887—88.*

(Concluded from p. 140).

Beer.

A.—*Methods of Investigation.*

By beer is to be understood a fermented and still fermenting drink, made from barley (or wheat), malt, hops, and water, and which was fermented by yeast.

I. *Determination of Specific Gravity.*—For this as well as all other determinations the beer is freed from carbonic acid, as far as possible, by half-filling bottles with it and shaking vigorously. It is then filtered. The specific gravity is then determined either by Westphal's balance or by a picnometer at 15° C.

II. *Determination of Extract.*—Seventy-five c.c. of beer are carefully weighed and evaporated in a suitable vessel to 25 c.c., care being taken to prevent boiling. After cooling water is added until the original weight is reached, and the specific gravity of the liquid taken as in I. The per cent of extract is obtained from this specific gravity by the use of a table constructed by Dr. Schultz, and is given as "per cent extract, Schultz."†

III. Alcohol is determined by distilling the beer. A piconometer of about 50 c.c. capacity and with a graduated neck is used as a receiver. The picnometer is carefully calibrated. 75 c.c. of beer are distilled until the distillate reaches about the centre of the scale on the picnometer. This is then cooled to 15° C., dried, and weighed, and the alcohol determined by means of Baumber's table.

$$A = \frac{D \cdot d}{g}$$

The percentage of alcohol by weight is to be given. In very acid beers it is necessary to neutralise before distilling.

IV. *Original Gravity of Wort.*—This may be ascertained, approximately, by doubling the per cent by weight of alcohol found, as above, and adding the per cent of extract. As this procedure is not exact, it may be made more nearly so by using the formula—

$$\frac{100\,(E + 2{\cdot}0665\,A)}{100 + 1{\cdot}0665\,A}$$

V. *Degree of Fermentation.*—This is estimated by using the formula—

$$V_1 = 100\left(1 - \frac{E}{c}\right)$$

VI. *Sugar Determination.*—This is to be determined directly, in the beer previously freed from carbonic acid, by Soxhlet's method of weighing the reduced copper; 1·13 parts of copper correspond to 1 part anhydrous maltose.

VII. Determination of dextrin is seldom required, and if required is to be performed by Sachsse's method.

VIII. *Nitrogen.*—Twenty to thirty c.c. are evaporated in a Hofmeister "schälchen" or on warm mercury, and the extract burned with soda-lime. The nitrogen may also be determined by Kjeldahl's method.

IX. *Acids.*—(*a*). Total acids:—The carbonic acid is driven off from 100 c.c. of beer by heating in beakers for a short time to 40° C., and the beer then titrated with baryta water (one-fifth to one-tenth normal). The saturation point is reached when a drop of the liquid has no longer any action on litmus paper. The acidity is to be given in c.c. normal alkali required for 100 grms. beer and as grms. per cent of lactic acid. The indication "acidity" or "degree of acidity" is insufficient.

(*b*). Normal beer contains but a very small quantity of acetic acid. The determination of fixed acid in the repeatedly evaporated extract is to be cast aside. The acetic acid produced by souring of the beer is shown by the increase of total acids. A qualitative test of the presence of acetic acid in the distillate from beers containing acetic acid is sufficient. Neutralised beer is to be acidified with phosphoric acid and distilled. Weigert's method is recommended.

X. *Ash.*—Thirty to fifty c.c. of beer are evaporated in a large tared platinum dish, and the extract carefully burned. If the burning takes place slowly, the ash constituents do not fuse together.

XI. *Phosphoric Acid.*—This is to be determined in the ash obtained by evaporating and burning in a muffle 50 to 100 c.c. of beer to which not too much baric hydrate has been added. The phosphoric acid is determined in the nitric acid solution of the ash by the molybdenum method.

XII. *Sulphuric Acid.*—The direct determination is not permissible. The determination is to be made by using the ash prepared by burning with sodic hydrate and potassic nitrate or baric hydrate and proceeding in the ordinary way.

XIII. *Chlorine.*—This is to be determined in the ash prepared with sodic hydrate.

XIV. *Glycerin.*—Three grms. calcic hydrate are added to 50 c.c. of beer, evaporated to a syrupy consistence, about 10 grms. coarse sea-sand or marble added, and

* Proceedings of the Fifth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, August 9 and 10, 1888.

† Hilger, p. 123.

dried. The dry mass is rubbed up, put into a capsule of filter-paper, placed in an extraction apparatus, and extracted for six to eight hours with 50 c.c. alcohol. To the light coloured extract at least an equal volume of ether is added, and the solution, after standing awhile, poured into or filtered into a weighed capsule. After evaporating the alcohol and ether, the residue is heated in a drying-oven at 100° to 105° C. to a constant loss of weight. In beers rich in extract the ash contained in the glycerin can be weighed and subtracted. In case the glycerin contains sugar this can be determined by Soxhlet's method and subtracted.

XV. Hop substitutes are to be determined by Dragendorff's method. Picric acid is to be determined by Fleck's method. In examining for alkaloids, check experiments with pure beer must, in all cases, be made.

XVI. *Sulphites.*—One hundred c.c. of beer are distilled after the addition of phosphoric acid, and the distillate conducted into iodine solution. After one-third has distilled over, the iodine-coloured distillate is acidified with hydrochloric acid, and baric chloride added. If sulphites are not contained in the beer no precipitate is observed, but at the utmost a turbidity.

XVII. *Salicylic Acid.*—This may be shown qualitatively by shaking with ether, chloroform, or benzine. The solution is allowed to evaporate, the residue dissolved in water, and a very dilute solution of ferric chloride added. The addition of too much acid and too violent shaking is to be avoided. The smallest trace of salicylic acid may also be shown by dialysis, as it passes very readily through membrane.

Note.—All the results of an investigation are to be stated in percentages by weight.

B.—*Methods of Judging Purity of Beers.*

I. It is unjust to demand in a fermented beer an exact ratio of alcohol to extract, as the brewer cannot regulate the degree of fermentation within narrow limits. As a rule, Bavarian draught and lager beers contain from 1·5 to 2 parts of extract for each part of alcohol, but a smaller proportion of extract would not necessarily prove the addition of alcohol or glucose (the former to the beer, the latter to the wort).

II. The degree of fermentation of a beer must be such that at least 48 per cent of the original extract has undergone fermentation.

III. If glucose or other bodies poor in nitrogen have been used in appreciable quantity as substitutes for malt, the nitrogen contents of the beer extract will fall below 0·65 per cent.

IV. The acidity of a beer should not be greater than 3 c.c. normal alkali to 100 c.c. beer. Acidity of less than 1·2 c.c. normal alkali to 100 c.c. beer indicates previous neutralisation. If the acids are composed principally of lactic acid a larger quantity may be present.

V. The ash of normal beer is not above 0·3 grm. to 100 grms. beer.

VI. The amounts of phosphoric and sulphuric acids and chlorine in beer extract vary within such wide limits, that their determination signifies nothing as to the purity of the beer.

VII. The amount of glycerin in pure beer is not greater than 0·25 grm. to 100 grms. beer.

VIII. The following methods of clarifying beer are legal:—(*a*). Filtration. (*b*). Well-boiled hazel or beech shavings. (*c*). Isinglass.

IX. The following methods of preserving beer are legal:—(*a*). Carbonic acid. (*b*). Pasteurising. (*c*). Salicylic acid; this only for beers intended for export to countries where the use of salicylic acid is not forbidden by law.

Note.—The preceding methods are also to be used in the examination of imported beer.

C.—*Administrative Note.*

It is absolutely necessary that the beer be preserved in well-corked green glass bottles. Stone jugs and such vessels are not to be used.

The beer samples are to be protected from light and kept at a low temperature.

Care in making tests is, above all, necessary.

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.*

By FRANK AUSTIN GOOCH and JAMES EDWARD WHITFIELD.

(Continued from p. 128).

Silica, Iron and Aluminum, Calcium, and Magnesium.—A single weighed portion of water served for the determination of silica, iron and aluminum, calcium and magnesium. The water was acidified with hydrochloric acid, evaporated to dryness in platinum over the water-bath, again acidified, and again evaporated. The residue was digested with hot water containing a little hydrochloric acid, and the solution was filtered from the residue of silica, which was ignited in platinum and tested as to its purity in the usual manner with hydrofluoric acid.

In the filtrate ammonia, in the slightest excess, precipitated ferric and aluminic hydrates from the boiling solution, and these were collected, ignited, and weighed as oxides in the usual manner. The lime was thrown out of the hot ammoniacal filtrate by ammonium oxalate, and the calcium oxalate filtered off after standing twelve hours in the cold. When the amount precipitated exceeded a few milligrms. it was dissolved in hydrochloric acid, reprecipitated by ammonia and ammonium oxalate, and collected upon a filter, the filtrate from the second precipitation being added to that from the first. The calcium oxalate was dried, ignited, and weighed as calcium oxide.

The filtrate (or the united filtrates) from the calcium oxalate was evaporated in platinum, and the residue was gently ignited to destroy the ammonium oxalate—which tends to delay the precipitation of the magnesia if permitted to remain in the solution—and dissolved in hydrochloric acid. From this solution the magnesia was precipitated in the usual manner by microcosmic salt and ammonia, and after standing twelve hours or more, the phosphate as collected upon asbestos in a perforated crucible, washed with the mixture of one part of ammonia to three of water, commonly used in the process, moistened at the end of the washing with a strong solution of ammonium nitrate in ammonia, ignited for a moment to redness, and weighed as the pyrophosphate.

Sodium, Potassium, and Lithium.—In some of the earlier work only sodium and potassium, of the alkalies, were determined in the natural water, and for the determination of the lithium portions of the concentrated water were treated by the method which will be referred to later. In the greater number of cases the same portion of the natural water served for the determination of the lithium as well as sodium and potassium. The portion for analysis was acidified in platinum with hydrochloric acid and evaporated to dryness. The residue was extracted with hot water slightly acidulated with hydrochloric acid, the solution was separated from the precipitated silica by filtration, and to the filtrate was added, with care to secure a sufficiency and yet to avoid a great excess, barium hydrate made from the nitrate, itself purified by precipitation by nitric acid. Filtration separated the precipitated hydrates of aluminum, iron, and magnesium, with barium

* *Bulletin o the United States Geological Survey*, No. 47.

sulphate; and from the filtrate ammonium carbonate and ammonia precipitated, upon boiling, nearly the whole of the barium and calcium as carbonates. The filtrate from the precipitated carbonates was evaporated to dryness, and the residue was gently ignited to remove ammonium chloride, treated with hydrochloric acid, freed from the excess of acid by evaporation on the water-bath to dryness, dissolved in a very small amount of water, and treated again with a few drops of the solution of ammonium carbonate and ammonia. This treatment usually results in the precipitation of traces of barium carbonate which have previously escaped removal by the similar treatment of the larger volume of liquid. The filtrate from this last slight precipitate was again evaporated and treated as before; and, in case any further precipitation took place, the process was repeated until the purification was complete. Usually, however, the first precipitation in the larger volume of liquid and the second treatment in the solution reduced to small bulk are together sufficient to remove the barium carbonate completely. The filtrate from the last precipitate was evaporated in a weighed platinum dish, and the residue, consisting of the chlorides of sodium, potassium, and lithium, was dried, gently ignited, and weighed.

From the mixed chlorides the lithium salt was separated by a process which, devised by one of us during the progress of the worked and described elsewhere in full,* needs but brief outlining in this place. To the concentrated solution of chlorides amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until, the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited, and the lithium chloride is dehydrated and taken into solution. At this stage of the proceeding the liquid is cooled, a drop or two of strong hydrochloric acid being added to re-convert traces of lithium hydrate possibly in the deposit, and the boiling is continued until the alcohol is again free from water. If the amount of lithium chloride present in the mixture of salts is small it is now found in solution; the chlorides of sodium and potassium, excepting the traces for which correction will be made subsequently, are in the residue; and the separation may be effected by filtration and the washing of the residue with amyl alcohol previously dehydrated by boiling. If, on the other hand, the weight of lithium chloride present exceeds ten or twenty milligrms. it is advisable, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the deposit, wash the latter with a little anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling in amyl alcohol.

The filtrates, first measured apart, are united with the washings and evaporated to dryness, and the residue, treated with sulphuric acid in excess, ignited gently at first and finally to the fusing point, is weighed as the neutral lithium sulphate, containing traces of the neutral sulphates of sodium and potassium. From the weight thus found the subtraction of 0·00109 g. for every 10 c.m.³ of filtrate exclusive of washings makes the proper correction for the amounts of the sodium and potassium salts present, and the residual weight represents the pure lithium sulphate. In cases where the precipitate consists solely of sodium chloride, the correction upon the weight of the sulphate is 0·00050 g.; when potassium chloride constitutes the residue the correction amounts to 0·00059 g. for every 10 c.m.³ of filtrate. The alcohol used in washing has, within reasonable limits, no appreciable solvent effect upon the precipitate.

The precipitate, consisting entirely of sodium chloride and potassium chloride, is ready for the balance after drying for a few minutes directly over a flame turned low, if the filtration is effected by means of asbestos in the perforated crucible; if paper is used as the filtering medium, after the solution of the precipitate, the evaporation of the solution and the gentle ignition of the residue. The weight of the insoluble chlorides actually obtained is corrected for the solubility of the salts in amyl alcohol by adding 0·00092 g. for every 10 c.m.³ of amyl alcohol in the filtrates, exclusive of washings; 0·00041 g. of this representing the sodium chloride dissolved, and 0·00051 g. the potassium chloride. With due attention to the reduction of volume of the residual alcohol before filtering the correction may be held easily within narrow limits.

In applying this method to the analysis of the waters of the Yellowstone Park the practice of reducing the volume of amyl alcohol to about 15 c.m.³ before filtering was followed uniformly. The corrections, therefore, were always the same, and amounted to an addition of 0·0007 g. to the apparent weight of sodium chloride, 0·0008 g. to that of potassium chloride, and a subtraction of 0·0017 g. from the weight of lithium sulphate indicated by the balance. In many cases the lithium present in the waters, though capable of detection by the spectroscope, amounted to so little in the portions devoted to its determination that the application of the correction left nothing to be called lithium sulphate. In such cases the lithium is counted as a "trace."

From the mixture of sodium chloride and potassium chloride the potassium salt was separated as potassio-platinic chloride. The chlorides were dissolved in a small amount of water, platinic chloride was added in solution, in quantity considerably in excess of the amount necessary to effect the conversion of all the potassium and sodium present to the double platinum salts, and the mixture evaporated on the water-bath to the point at which the residue becomes pasty if removed from the bath and allowed to cool. The crust thus formed was drenched with alcohol of 80 per cent., digested in the cold until thoroughly disintegrated, filtered off on an asbestos felt, washed with alcohol of 95 per cent, dried at a gentle heat, and weighed.

The lithium and potassium having been thus found directly, the sodium is given, in the form of the chloride, by the difference between the sum of the lithium and potassium chlorides and the total weight of the three chlorides; or, by the difference between the weight of potassium chloride found and the weight of the chlorides of potassium and sodium found (the proper correction having been applied) after the separation of the lithium. It may be urged against the former plan that to bring the three chlorides to a definite condition for weighing is a difficult undertaking in view of the great tendency of lithium chloride to exchange chlorine for oxygen in the presence of water. Our experiments indicated, however, that under repeated treatments by moistening and ignition the mixed chlorides did not change in weight materially, and we are disposed to attribute the result in part to the protective influence of the sodium and potassium salts upon the relatively small amount of lithium chloride, and in part to the care taken to secure thorough drying at a low temperature previous to the gentle ignition. In our work upon the waters we weighed the three chlorides together and found the sodium chloride by deducting from this weight the weights of potassium chloride and lithium chloride deduced by analysis.

A weak point in the process which we have employed in the determination of the alkalies would seem to be found in the separation of the magnesia by means of barium hydrate. In connection with this subject it is of interest to note that in the greater number of waters magnesia was present only in inconsiderable quantity, and further, that in the case of those in which it did appear in appreciable amounts the examination of the solution of the lithium sulphate, after the separation by amyl alcohol, failed to indicate the presence of magnesia in amount sufficient to be precipitable by microcosmic salt in an ammoniacal solution and under the usual conditions of the test, though this would be the place in

* *Bulletin of the U.S. Geological Survey*, No. 42, p. 73; *Am. Chem Jour.*, vol. 9, p. 33.

which magnesia should appear if it had escaped removal from the chlorides. We are constrained to believe, therefore, that the process of separation which we adopted was exact within reasonable limits.

Ammonia and Albumenoid Ammonia.—The determination of ammonia was effected in the usual manner by distilling a measured portion of water with sodium hydrate, and nesslerising the distillate. A second portion of water was distilled with sodium hydrate and potassium permanganate, and the distillate was nesslerised. The former process gives the combined ammonia present in the water; the latter the total ammonia, which includes, besides the ammonia existing as such in combination, that ammonia which is developed from other nitrogenous compounds by the action of the permanganate. The difference between the figures of the two processes is the albumenoid ammonia, so called. The composition of these waters renders them peculiarly liable to boil explosively, and some difficulty was experienced at first in the distillation; but the apparatus which is described in the paragraph on the determination of the boric acid proved to be of service in this case also, and made the determination practicable. The Nessler solution was very delicately adjusted, and the tests were made in small tubes and carried to the limit of 0·000001 g.

Treatment of Concentrated Waters.

In the examination of the concentrated waters the whole sample was evaporated to dryness, and the residue thus left was extracted with hot water. It is usual in treating concentrated waters to add sodium carbonate during the evaporation, and to wash the residue until the washings cease to show an alkaline reaction. Four of the waters of which we had concentrated samples were, however, so alkaline of themselves that the addition of sodium carbonate was superfluous, and all were so siliceous that to wash the residue of evaporation until it was free from alkali was a matter of the greatest tediousness and difficulty. We found it best and sufficient to wash only to the vanishing point of the spectroscopic reaction for lithium in the washings. In this manner the separation of the greater part of the silica with the insoluble constituents of the water was effected without an entirely unreasonable expenditure of time and effort. The filtrate and washings were thoroughly mixed and made up to a definite weight. The residue was kept by itself for separate treatment.

The filtrate should contain the bromine, iodine, boron, arsenic, antimony; the copper, lead and tin, which can be present in the waters only in traces; the lithium, cæsium, rubidium, thallium, and part of the silicon and aluminum. The precipitate should contain the titanium, phosphorus, fluorine, iron, manganese, barium, strontium, calcium, magnesium, with the remainder of the aluminum and silicon.

Strength of the Concentrated Waters.

The degree to which the concentration of the waters had been carried in the field was fixed by the determination of the total amount of halogens in a weighed portion of the extraction of the residue of evaporation. This portion was diluted, acidified with nitric acid, treated with silver nitrate until the precipitate ceased to form, and the last was collected on asbestos in a perforated crucible, dried (over the free flame of a Bunsen burner turned low) at a temperature considerably below its melting point, and weighed. Determinations of this sort were made in duplicate. Knowing the weight of the silver salt thus found and the weight of the same precipitable from a known weight of the natural water, the exact value of the concentrated water, in terms of the natural water which it represented, became known.

Treatment of the Residue.

Fluorine.—The residue, dried by gentle heating, with the ash of the filter employed in separating and washing it, was placed in a retort of the pattern described in the section treating of the determination of boric acid in the natural water, drenched with strong sulphuric acid, and heated to 150° C., while a slow current of dry air was forced through the emulsion and thence directly into a U-tube partly filled with dilute ammonia. The fluorine contained in the water should appear in the residue as calcium fluoride, should be volatilised as silicon fluoride by the action of the sulphuric acid, and, if present in more than very small amounts, should be indicated by the precipitation of silica in the U-tube containing ammonia. Proceeding in this manner we found in the waters which we examined no fluorine; and on treating the ammoniacal liquid of the U-tube according to the method of Berzelius, with zinc oxide dissolved in ammonia, evaporating until the solution ceased to evolve ammonia, filtering, adding to the filtrate calcium chloride followed by sodium carbonate, boiling, igniting the precipitate and extracting it with acetic acid, we were not able to detect a residue of calcium fluoride: nor in the zinc oxide precipitated by the expulsion of the ammonia dissolving it could we discover silica.

Barium and Strontium.—The contents of the retort were transferred to platinum, treated with hydrofluoric acid (purified by re-distillation) in sufficient amount to volatilise all silica, and evaporated to dryness with a little sulphuric acid. To insure thoroughness of action this process of treatment was repeated. The residue was fused with sodium carbonate and the melt was extracted with hot water containing a few drops of alcohol. The precipitate was separated from the solution by filtration and digested with hot dilute acetic acid, which should dissolve the barium, strontium, calcium, and magnesium carbonates. The solution in acetic acid, separated by filtration from the portion unacted upon, was nearly neutralised with ammonia, and to it was added in solution an amount of ammonium sulphate equal to fifty times the weight of the alkaline earths present, the whole being permitted to stand quietly twelve hours. By this treatment barium and strontium should be precipitated as sulphates, while calcium and magnesium should remain dissolved. The sulphates of barium and strontium may be separated afterward by digestion during twelve hours (at the ordinary temperature and with frequent stirring) in ammonium carbonate, the decantation of the supernatant liquid, the repetition of the treatment with ammonium carbonate, and, finally, the action of hydrochloric acid upon the residue—the strontium carbonate dissolving and the barium sulphate remaining insoluble in this acid. This mode of separating the barium and strontium was not actually applied in our work, inasmuch as we obtained from the quantities of water with which we had to deal no precipitate by ammonium sulphate, and it is mentioned only for the purpose of completing the scheme of analysis.

The solution which had been treated with ammonium sulphate to precipitate barium and strontium was preserved for subsequent examination for manganese.

Phosphoric Acid.—The extract of the fusion in sodium carbonate was acidified with nitric acid, evaporated to small bulk, and from it the phosphoric acid was precipitated in the usual manner as a phosphomolybdate of ammonia. The precipitate, after standing twelve hours, was separated by filtration through a felt of asbestos in a perforated crucible, washed with the precipitant, and dissolved in ammonia. From this solution the phosphoric acid was precipitated by the magnesium and ammonium chloride mixture, and the ammonio-magnesium phosphate was filtered off on asbestos, washed with dilute ammonia (one part of ammonia to three of water), moistened with ammonium nitrate in ammonia, dried, ignited at a red heat, and weighed as magnesium pyrophosphate.

Manganese.—The residue left, after the extraction of the fusion in the sodium carbonate with water containing a little alcohol and the treatment with acetic acid, was fused again in a little sodium carbonate, the melt was

dissolved in the crucible by heating with strong sulphuric acid, and this solution was poured into cold water. In this manner was obtained a solution containing the titanium and iron, and a part of the aluminum and manganese. From it all these elements, excepting the last, were precipitated by adding ammonia to an alkaline reaction followed by acetic acid to faint acidity, and boiling. The precipitate was kept for examination later. The solution was mixed with that which had been treated with ammonium sulphate in the test for barium and strontium, and to the mixture, heated on the water-bath, were added ammonia in excess and bromine water. The precipitate thus obtained was ignited and weighed as Mn_3O_4, it being so trifling that solution and re-precipitation as the phosphate was unnecessary.

Iron.—The precipitate of ferric, titanic, and aluminic hydrates was fused in a little sodium carbonate, the fusion was dissolved in strong sulphuric acid, this solution poured into cold water, and the dissolved iron, titanium, and aluminum were separated as follows, by a process devised by one of us and described fully elsewhere.* Tartaric acid, amounting to three times the weight of the oxides of iron, aluminum, and titanium present, was added to the solution, which was then made faintly ammoniacal and submitted to the action of a current of hydrogen sulphide. The precipitated ferrous sulphide was filtered off (care having been taken that the solution should still be alkaline before filtering), washed with hot water sufficiently but expeditiously, dissolved in hydrochloric acid, and the iron, first oxidised by bromine, was precipitated by ammonia and weighed as the oxide.

Titanic Acid.—The filtrate from the ferrous sulphide was acidified strongly with sulphuric acid, heated to the boiling point, and treated with potassium permanganate until its characteristic colour appeared. The final products of the action of the permanganate upon the tartaric acid are carbonic acid and water, but formic acid appears as an intermediary step in the oxidation. During the first action of the permanganate its conversion to manganous sulphate is rapid, but with the development of formic acid there takes place by its action upon the permanganate freshly added a precipitation of a brown hydrate of manganese, which, re-dissolving readily so long as tartaric acid remains, yields only slowly to the further action of the formic acid. When, therefore, manganic hydrate appears abundantly in the boiling solution and does not dissolve perceptibly, one may be reasonably certain that the conversion of the tartaric acid to at least the intermediary stage has been accomplished; but for the sake of greater security, the addition of the permanganate may be continued until the appearance of its colour. When the amount of tartaric acid in the solution is known, as should be the case always, a simple mode of proceeding is, perhaps, to employ for the oxidation the amount of permanganate theoretically required. A weight of potassium permanganate amounting to two and a half times the weight of the tartaric acid to be destroyed is sufficient to carry the oxidation to the ultimate limit, providing there be no deposition of a manganic hydrate.

The residual permanganate and the insoluble hydrate were reduced and dissolved by the addition of a little ammonium bisulphite to the acid solution, and, the excess of sulphurous acid having been boiled off, acetic acid was added to the clear solution in quantity sufficient to make the amount of the absolute acetic acid present from 7 to 11 per cent by volume; enough sodium acetate was introduced to fix all the sulphuric acid as sodium sulphate, and the solution was boiled. If titanium is present it is precipitated under these conditions, while the aluminum remains dissolved. If the quantity of the precipitate thus obtained is considerable, it should be filtered from the liquid in which it floats, and purified from the traces of manganese which it may carry by fusion in a small quantity of sodium carbonate, the solution of the melt in sulphuric acid, and re-precipitation by ammonia.

In the waters which we examined we found no precipitate of titanic hydrate at the point in the process where it should appear were titanium present.

(To be continued).

* *Bulletin of the U.S. Geological Survey*, No. 27, p. 16; *Am. Chem. Jour.*, vol. vii., 1885—1886, p. 283.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 20th, 1888.

Mr. William Crookes, F.R.S., President, in the Chair.

Mr. Frank Bower was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. P. Carmody, F.I.C., The Laboratory, Somerset House; Edward Mitchell Chaplin, Westgate, Wakefield; John Curragh, Donaghadee, Belfast; David Ferrier, The Cottage, 50, High Street, Montrose; Conrad Gerland, Church, Lancashire; Alfred Miall Hanson, The Marjorie, Whalley, near Blackburn; Henry Joshua Phillips, Great Western Railway Laboratory, Swindon; Thomas John Underhill, 43, Chapel Road, West Norwood, S.E.

The following papers were read:—

96. "*On some Leadhills Minerals.*" By Norman Collie, Ph.D.

Up to the present time the analyses of the rare lead minerals which are to be found at the Leadhills in the southern highlands of Scotland have been both meagre and contradictory. The author communicates a number of analyses of some specimens of leadhillite, lanarkite, vanadinite, and other minerals, obtained from Dr. Wilson, of Wanlock-head, Leadhills, and also of a considerable number collected by himself. The investigation was undertaken for two reasons; the chief one being to ascertain whether in the large number of double carbonates, sulphates, phosphates, &c., found at Leadhills, the constituent salts were always present in molecular proportions, or whether they were only isomorphous mixtures. The other reason was to determine which among the conflicting analyses met with in the mineralogical treatises were the most probably correct. Two new minerals were met with:—(1) A pyromorphite, containing both copper oxide and vanadic acid; (2) an aragonite in which part of the calcium carbonate had been displaced by lead carbonate.

The other minerals analysed were leadhillite, lanarkite, caledonite, linarite, vanadinite, pyromorphite, plumbocalcite, calamine, dolomite, and strontianite.

97. "*Metallic Derivatives of Halogen Nitrophenols.*" By Arthur R. Ling.

Chlorobromoparanitrophenol, prepared by brominating chloroparanitrophenol, m. p. 110°, in acetic acid solution, separates from boiling water in colourless crystals melting at 137° with decomposition. The following metallic derivatives of this phenol are described:—

Potassium salt, $C_6H_2ClBrNO_3K\cdot H_2O$, golden-yellow needles.

Calcium salt, $(C_6H_2ClBrNO_3)_2Ca\cdot 9H_2O$, yellow needles.
" $(C_6H_2ClBrNO_3)_2Ca\cdot 4H_2O$, yellow plates.

Barium salt, $(C_6H_2ClBrNO_3)_2Ba\cdot 10H_2O$, yellow needles.
" $(C_6H_2ClBrNO_3)_2Ba\cdot 3\frac{1}{2}H_2O$, red needles.

The calcium-derivatives of the following were also examined:—

Dibromorthonitrophenol, red plates, containing 7 mols. H_2O.

Dichlororthonitrophenol, orange-yellow fibrous needles, containing 1 mol. H_2O.

Dichlororthonitrophenol, red crystals, containing 4 mols. H_2O.
Parachlororthobromorthonitrophenol, red plates, containing $4H_2O$.
Parabromorthoiodorthonitrophenol, red plates, containing $4H_2O$.

They are almost insoluble in cold and only sparingly soluble in boiling water.

A general feature of the calcium-derivatives of the nitrophenols, especially those of the orthonitro-series, seems to be the difficulty with which the water of crystallisation is removable on heating, *e.g.*, it was found impossible to completely dehydrate calcium dibromorthonitrophenol below a temperature at which it decomposed. The author also points out that as they lose their water of crystallisation, the calcium orthonitrophenol-derivatives change from red to an orange colour, which is at variance with the conclusions of Carnelley and Alexander.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 10, March 11, 1889.

Oxygenated Water and Chromic Acid; New Experiments.—M. Berthelot.—In a former paper the author has established that the reactions of hydrogen peroxide and chromic acid may be produced also if potassium dichromate is substituted for chromic acid. The unlimited decomposition of oxygenated water by this salt is due to the formation of an intermediate compound, which is incessantly formed and reproduced. This intermediate compound, which turns the liquid brown, has some such composition as—

$$nCr_2O_3CrO_3+3HO_2.$$

Use of Sodium Sulphite in Photography.—Paul Poire.—From a great number of experiments it results that with commercial sulphites it is always advantageous to take as a developing-bath a solution of sodium sulphite at 25 per cent, to which is added 1·5 grms. per cent of pyrogallic acid. There is no need to add carbonate unless the development is too slow.

A Small Portable Apparatus for the Easy and Safe Production of the Magnesium Flash.—Ad. Guébhard and P. Ranque.—The authors give a series of figures illustrating their apparatus.

On the α- and γ-Mono-chlor-acetoacetic Ethers. An Attempt at the Synthesis of Citric Acid.—A. Haller and A. Held.—This paper does not admit of useful abstraction.

Researches on Australene.—Ph. Barbier and J. Hilt.—Australene is an extract from the oil of turpentine of *Pinus australis* of South Carolina. It is a colourless liquid, very mobile, and of a slight odour. Its sp. gr. at 0° is 0·8789. Its rotatory power is $[\alpha]_D = +22·85°$. If heated for two hours to 300° it is changed into the corresponding isoterebenthene.

The Influence of Thiophene and its Homologues upon the Colouration of the Derivatives of Benzene and its Homologues.—A. Bidet.—Nitrobenzene, even if prepared from crystalline benzene, always presents, after several distillations, a yellowish tint, which deepens under the influence of light. If we use benzene freed from thiophene the nitrobenzene obtained, even on the first distillation, has merely a slight yellowish green tint, which is not affected by light. The addition of a single crystal of mono-nitro-thiophene restores to pure nitrobenzene the properties of ordinary nitrobenzene. Toluene, if freed from thiotoluene by processes similar to those used in the purification of benzene, is similar in colour to pure nitrobenzene. Phenol, prepared by means of a sulphone freed from thiophenic compounds, may be obtained in fine colourless needles, which do not turn yellow or red, even after months of exposure to light. The pure nitro-compounds may be converted into amines, and then the aniline or toluidine does not acquire that deep red-brown colour which the ordinary products always acquire after a time If we stop the purification of benzene at the moment when we can no longer trace a blue colouration with isatin we have still a nitrobenzene, which turns yellow, and the aniline derived from it takes the characteristic brown tint. Aniline, ortho-, and para-toluidine, if freed from thiophenic compounds, and being in suitable proportions to form "aniline for reds" yield merely traces of magenta on treatment with syrupy arsenic acid. The same amines, if prepared from pure materials, but to which nitrothiophene has been added before reduction, yield a red colouring-matter, exactly as does ordinary aniline for reds.

The Fertilising Properties of the Waters of the Nile.—A. Müntz.—It has been already demonstrated that the waters of the Nile owe little of their fertilising power to the presence of nitrates. The water of the Nile in time of flood in September contains per cubic metre:—

	Dissolved.	Suspended.
Nitrogen..	1·07 grms.	3·00 grms.
Phosphoric acid ..	0·40 ,,	4·10 ,,
Potash	3·66 ,,	150·00 ,,
Lime	48·00 ,,	70·50 ,,

Hence the mud is the main fertilising agent.

The Slow Combustion of Certain Organic Matters.—Th. Schlœsing, Jun.—The author, referring to a former paper on the slow combustion of tobacco and the part played in it by micro-organisms at different temperatures, extends researches of the same kind to dung. Lots of dung were first sterilised by heating for an hour to 115°, after which some of them were sown with a little of the drainings or the dust of fresh manure, whilst the others remained secluded from external germs. At 75·5° the portion treated with germs evolves fifteen times as much carbonic acid as simple chemical combustion.

Moniteur Scientifique, Quesneville. March, 1889.

Bleaching Cotton Tissues: the Saponification of Fatty Bodies upon the Fibre, followed by Observations Exerted by the Process of Bleaching upon the Oxides of Various Metals Previously Fixed upon the Fibre.—Albert Scheurer.—This memoir is taken from *Bulletin de la Société Industrielle de Mulhouse* and is too extensive for insertion. M. Scheurer considers that the great novelty of the Mather and Platt process consists rather in its mechanical arrangements than in the chemical operations which it renders admissible.

Researches on Narcotin.—This paper, taken from *Liebig's Annalen*, does not admit of abstraction.

On Tartar Emetic.—Professor Dunstan and Miss L. E. Boole.—From the *Pharmaceutical Journal.*

The Examination of Commercial Phenol, and of Phenic Disinfecting Powders.—Rowland Williams.—From the *Journal of the Society of Chemical Industry.*

On New Explosive Substances.—This paper contains a description of Favier's explosive, a mixture of mononitronaphthaline with ammonium nitrate, enclosed in an envelope composed of the same substances mixed with 4 per cent of paraffin. Then follows an account of the "Flameless Powder," invented by Schœneveg, of Dudweiler, and worked on a large scale by the "Flameless Explosives Company," of London. It is possible

identical with the substance known under the barbarous name "Grisoutite." It is alleged to be incapable of igniting explosive mixtures of gases, or air holding coal-dust in suspension. It is described as consisting of explosive gelatin mixed or coated with oxalic acid or oxalates, in order both to increase its shattering power and to prevent spontaneous combustion and the production of flame. Romite, the invention of Sjoeberg, consists of two portions which are afterwards mixed together. One of these consists of ammonium nitrate, naphthaline, and rectified paraffin oil; the other mixture is composed of potassium chlorate, naphthaline, and paraffin oil. The Carbodynamite of W. D. Borland is essentially nitroglycerin absorbed in the charcoal of cork, or a mixture of the latter substances with kieselguhr and soda-ash.—*Chemische Industrie.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Estimating Carbon in Steel.—In Eggertz's colouration process for estimating carbon in steel the colour of steel solutions is darkened by heating in boiling water. How is this? Should the estimation and comparing of the colours be conducted warm or cold?—YOUNG ANALYST.

MEETINGS FOR THE WEEK

MONDAY, April 1st.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.
—— Society of Chemical Industry, 8. "The Action of Water on Lead," by Dr. P. F. Frankland. "Economy of Pure Caustic Soda," by Messrs. Cross and Bevan.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 2nd.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Sanitary Institute, 8. "Infectious Diseases and Methods of Disinfection," by Shirley F. Murphy.
—— Society of Arts, 8. "The Argentine Republic," by F. K. Smythies.
—— Pathological, 8.30.
WEDNESDAY, 3rd.—Society of Arts, 8. "Fruit Growing for Profit in the Open Air in England," by W. Paul.
—— Geological, 8.
THURSDAY, 4th.—Royal, 4.30.
—— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
—— Chemical, 8.
FRIDAY, 5th.—Royal Institution, 9. "True and False Humour in Literature;" by the Rev. Canon Ainger.
—— Geologists' Association, 8.
—— Sanitary Institute, 8. "General Powers and Duties of Inspectors of Nuisances—Method of Inspection," by J. F. J. Sykes, B.Sc.
SATURDAY, 6th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that LEOPOLD CASELLA AND COMPANY, of Frankfort-on-the-Main, Germany (Assignees), have applied for leave to amend the Specification of Letters Patent No. 9214 of 1885 granted to Meinhard Hoffmann and Arthur Weinberg, both of Mainkur, near Frankfort-on-the-Main, in the Empire of Germany, for "The production of new azo-colours."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 20th March, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed) H. READER LACK, Comptroller-General.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1532.

RELATIVE AMOUNTS OF VOLTAIC ENERGY OF DISSOLVED CHEMICAL COMPOUNDS.*

By G. GORE, LL.D., F.R.S.

In this investigation the author has measured, by the "voltaic balance" method, the amounts of relative voltaic energy or of chemical affinity for zinc of nearly 250 aqueous solutions of chemical compounds; including those of elements with elements; elements with monobasic, bibasic, and tribasic acids; acids of all these classes with each other; elements with monobasic, bibasic, tribasic, and tetrabasic salts; monobasic, bibasic, and tribasic acids with all these classes of salts; and all these classes of salts with each other in large variety; and he offers the results as additional evidence in support of the conclusion that "*every electrolytic substance or mixture, when dissolved in water, unites chemically in definite proportions by weight with every other such dissolved body*," provided no separation of substance occurs;" and that "there may probably be discovered thousands of such compounds, which only exist whilst in aqueous solution, and are decomposed on evaporating or crystallising their solutions" (*Roy. Soc. Proc.*, vol. xliv., p. 267). The results are given in the form of a volta tension series of electrolytes.

NOTE ON A SAMPLE OF PALMITIC ACID.

By J. C. A. WILSON.

Some time ago the author had reason to examine a sample of white palmitic acid. On examining it for the iodine equivalent it gave 25 per cent, corresponding to 28 per cent oleic acid approximately. The mean combining weight was 265, and the melting-point 48 Centigrade. On carefully treating it by the process depending on the solubility of the lead salt in ether, it gave 2 per cent oleic acid.

These results are very paradoxical, and I may point out the statement of Benedict, who found distilled stearic acid absorbing 14 per cent iodine to yield no oleic acid on treating the lead salts with ether.

In connection with this may be mentioned the fact that J. C. A. Wilson and M. Satzeff (*Jour. Prak. Chem.*, xxxvii., 269) find oxystearic acid to be converted into isoleic acid on distillation, melting at 43° C.

The Laboratory, Tottington,
March 27, 1889.

ESTIMATION OF INSOLUBLE PHOSPHATES.

By VINCENT EDWARDS, F.C.S.

The following short and simple method of estimating the insoluble phosphate in superphosphates, &c., may be of interest to your readers, especially to manure works chemists, who are frequently required to test a sample of manure at a short notice:—I treat five grms. in the usual way, and test the water solution for soluble phosphate; the residue filter, and all is then dissolved with dilute HCl and $4NO_3$ in a beaker placed in a water-bath; about half an hour will suffice to dissolve out all the phosphates; the solution is then filtered, 20 c.c. of a solution of phosphates of lime in dilute nitric acid added (about 5 grms. $Ca_3P_2O_8$ to the litre is a good strength), and the whole made up to 250 c.c.; 50 c.c. of this solution = 1 grm. is taken, ammonia added till alkaline, made acid with acetic acid, and then titrated with uranium solution—being heated to boiling on the first addition of the uranium. The strength of the added phosphate of calcium being known, the quantity of uranium required to precipitate one-fifth of it is deducted from the result. I have found this plan very useful when the sample contains large quantities of gypsum, and when the results are required in a few hours after the mixing is made up. An allowance must be made for iron and alumina, but this can be determined accurately once for all, and the amount will not vary much. I generally add 0·5 per cent for phosphate in combination with these matters.

The Laboratory,
Wicklow Chemical Works,
March 26, 1889.

GYMNEMIC ACID.

By DAVID HOOPER, F.C.S., F.I.C.

Some years ago it was discovered by Mr. Edgeworth that the leaves of *Gymnema sylvestre* had the peculiar property of destroying the power of the tongue to appreciate the taste of sweet substances. In the early part of 1887 Sir M. E. Grant Duff, then Governor of Madras, interested himself in the subject, and forwarded me from his grounds in Grundy Park a supply of the leaves for investigation. A paper containing the results of a chemical examination, with their proximate analysis, has already been published,* and now some notes are sent relating to the chemistry of the principle possessing this singular property, which was discovered at that time.

Gymnemic acid exists in the leaves in the form of a potassium salt, and is best prepared by treating the aqueous solution of the alcoholic extract with a mineral acid, washing the precipitate, and drying in a current of hot air or over a desiccator.

The acid is a brittle black resinous substance of a greenish colour when reduced to powder. It is insoluble in water, soluble in alcohol (with an acid reaction), ether, benzol, and chloroform, and slightly in amylic alcohol and carbon bisulphide. With potash, soda, and ammonia it affords fine red solutions with an orange-coloured froth, and precipitated on the addition of acids. It dissolves in concentrated sulphuric and nitric acids with intense red colour, and in both mixtures it is destroyed and precipitated by water. Prolonged contact with nitric acid forms a soluble nitro-compound or product soluble in water. It fuses at about 60° C. into a black liquid of thick consistence; above 100° it gives off creosotic fumes, and, at a higher temperature, burns with a bright smoky flame, leaving no ash. It is thrown down as a bulky grey mass with plumbic acetate, and the lead salt may be decomposed by hydrogen sulphide in the presence of spirit. It is also precipitated by ferric chloride, silver nitrate, barium and calcium salts, but not by tannin, picric acid, and gelatin solution. It forms insoluble salts with alkaloids, and this accounts for its masking the taste of quinine and other bitter substances.

The acid, dried at 100° C., was submitted to combustion with cupric oxide.

(*a*). 0·2152 grm. gave 0·4807 grm. CO_2 and 0·1706 grm. H_2O.
(*b*). 0·2738 ,, 0·6080 ,, ,, ,,

From these experiments may be deduced the empirical formula $C_{32}H_{55}O_{12}$; the re-calculation of the elements from such a formula shows a close correspondence with the mean percentage found.

* Abstract of a Paper read before the Royal Society, March 14, 1889.

* *Nature* and *Pharm. Journ. and Trans.*, April, 1887.

	(*a*).	(*b*).	Mean.	Calculated for $(C_{32}H_{50}O_{13})$.
Carbon	60·92	60·55	60·73	60·85
Hydrogen ..	8·80	8·61	8·71	8·71
Oxygen	30·28	30·84	30·56	30·44
	100·00	100·00	100·00	100·00

The silver salt of gymnemic acid is a black brittle powder; it afforded 14·02 per cent of metal on combustion. Theory for $C_{32}H_{54}O_{12}Ag$ requires 14·63 per cent of metallic silver.

Gymnemate of lead is insoluble in acetic acid, and forms a black uncrystallisable powder. A weighed portion of the dried salt gave 15·19 per cent of plumbic oxide. Theory for $(C_{32}H_{54}O_{12})_2Pb''$ requires 15·20 per cent of PbO.

There is evidence that gymnemic acid is a monatomic acid from the compositions of its silver and lead salts, and its molecular weight, 631, agrees with its power of saturating alkali. It was found by experiment that 0·631 grm. of the acid, treated with centinormal solution of caustic soda, did not strike a red colour with phenolphthalein until sufficient solution, equivalent to about 0·040 grm. of NaHO, had been added.

I have not obtained the acid or its salts in anything approaching a crystalline condition; they dry as do tannic acid and the tannates. Ammonium gymnemate exhibits the characters of the drug better than other salts.

The acid is a glucoside. After boiling for about an hour with dilute hydrochloric acid a dark resinous mass, devoid of the peculiar property of gymnema leaves, remains, and the liquor contains a body which readily reduces Fehling's solution.

Gymnemic acid occurs in other species of *Gymnema* besides *sylvestre*. *G. hirsuta* contains a considerable quantity, and *G. montanum* leaves contain it in a smaller proportion.

Ootacamund, India.

VOLUMETRIC ESTIMATION OF NICKEL.

By THOMAS MOORE.

The process which I now describe is one based on the results of a large number of experiments carried out with the object of finding a volumetric method, to be at once sufficiently rapid and accurate for all practical purposes. The principle finally selected is that of the formation of the double cyanide of nickel and potassium in alkaline solutions by the addition of potassic cyanide. It is, however, impossible to judge of the end of the reaction by the disappearance of the blue colour, owing to the production of a yellowish tint which effectually conceals any further change, so that recourse must be had to indicators. In the first experiment excess of potassic cyanide was added, and this excess titrates back in neutral solution by iodine and starch, but in no case could a distinct blue be obtained. Titration of excess of cyanide by argentic nitrate is inadmissible, since the nickel compound is decomposed thereby. If, however, a small quantity of cupric ferrocyanide is added to the ammoniacal solution of nickel, then the potassic cyanide, no alteration in colour will take place with the copper compound until the nickel is completely converted into the double cyanide, and a very small quantity of potassic cyanide over and above what is required immediately destroys the copper salt, and the solution undergoes a distinct change in colour, thus indicating the end of the reaction.

A considerable number of experiments made with the process (checked by comparison with the figures obtained by electrolytically depositing the nickel) have amply proved that it is reliable and quite accurate enough for all ordinary purposes.

Solutions.—Potassic cyanide (pure): 22·5 grms. per litre. 20 c.c. of this are equal to about 0·1 grm. nickel. Cupric ferrocyanide: dissolve 2·25 grms. of cupric sulphate in one litre of water, and add a solution of potassic ferrocyanide until it ceases to produce any further precipitation. Thoroughly agitate before use.

Process.—If the solution contains much free ammonia, as in the filtrate from iron and nickel separation, neutralise part of it by addition of hydric chloride; if acid, add ammonia until strongly alkaline, then run in the potassic cyanide from a burette, stirring continually until the blue colour completely disappears and the solution takes a yellowish tint; when this happens add a measured quantity of cupric ferrocyanide sufficient to impart a distinct colour to the solution; the amount required for this purpose is variable, and depends upon the free ammonia present; now add the cyanide more cautiously, until finally one drop causes a distinct change of colour in the solution. A little practice is necessary to recognise the change, but after a few trials no difficulty will be experienced. The amount of cyanide necessary to decolourise the copper salt is so small that it may often be neglected; but if desired, the error may be eliminated by ascertaining how much cyanide is necessary to decolourise 100 c.c. of the copper solution, and reckoning out the difference in the usual way. Of course it is first necessary to standardise the cyanide solution with one of nickel of known strength.

The process gives equally good results in the presence of sulphates, nitrates, chlorides, or acetates, also in the presence of large quantities of ammoniacal salts, but large quantity of free ammonia should be avoided, owing to the solubility of the cupric ferrocyanide therein.

Appended are a few of the results obtained compared with those found electrolytically in different ores.

Electrolytically.	Volumetrically.
6·55 per cent Ni.	6·49 per cent Ni.
8·60 ,,	8·70 ,,
6·35 ,,	6·37 ,,
9·55 ,,	9·60 ,,
7·85 ,,	7·77 ,,

Thio, New Caledonia,
February 8, 1889.

NOTES ON RECENT AND FUTURE RESEARCH.

By SAMUEL E. PHILLIPS.

We have long considered ammonia as the indifferent or non-carbonising hydride of the radical "amidogen," H,H_2N, and that $A=(NH_2)$ would probably be a 1 vol. representative of H, as so familiar in the teeming amido-compounds.

A recent number of *Nature* announces the discovery by Dr. Theodor Curtius, "who has succeded in preparing the long sought for hydride of N, 'amidogen.' This remarkable body has hitherto baffled all attempts at isolation," &c.

The Doctor is apparently a victim to a very common abuse of "Avogadro-law," which has greatly marred and confused his achievement. As H is one vol., and its hypothetic molecule, H_2, 2 vols; so it may be, and is, with other radicles of H equivalence. When the methyl body, "silico-methyl," was discovered, and found to be 1 vol., its 2 vol. molecule would be either $(Si_2E_3)_2$ or (Si_4E_6), but surely there is nothing in "Avogadro-law" to make it the latter rather than the former. But this is just the abuse I complain of, and mad theory contends that it is of ethane rather than methyl constitution, as "di-silico-hexethyl." However, Ladenburg, as a man of genius and a great chemist, speaks only of "silico-triethyl" in his lucid picture of the methyl-derivatives.

Cacodyl is another case, and one of amidogen type $(AsMe_2)$. As it ought to be, so it is, 1 vo., whereupon

theory steps in, and declares it not to be $(AsMe_2)_2$ but (As_2Me_4); but they are compelled to admit that with chlorine it splits into "two atoms of cacodyl chloride," $(AsMe_2)C_2$.

In like manner Dr. Curtius makes the *molecule* of amidogen to be not $(NH_2)_2$, but—

$$\begin{matrix} NH_2 \\ | \\ NH_2 \end{matrix}$$

and then speaks of it as "amidogen or hydrazine, as it is variously called."

Who then are the culprits? I have never seen the two things thus confused. This reminds me that a great deal too much value is assigned to this 2 vol. law. Here we have hydrazine, $A,H_2N = 2$ vols., and 2 atoms of amidogen, $(NH_2)_2$, 2 vols., both containing the same number of elements, where *the law* is powerless in that discrimination, which chemism is so well fitted to supply. One is an ammonia with a whole train of plain consequents. The other is a radical evincing wholly different characters. One combines with H chloride to form, not a *hydrochloride*, but a chloride of ammonium. The other does nothing of the kind, and the hydrate of the text is utterly anomalous, and inapplicable to amidogen.

His "hydrate of amidogen" =

$$N_2H_4{\cdot}H_2O = AH_3N,O{\cdot}HO.$$

His "dihydrachloride" =

$$\left.\begin{matrix} NH_2{\cdot}HCl \\ | \\ NH_2{\cdot}HCl \end{matrix}\right\} = AH_3N,Ce{\cdot}HCl.$$

And the "monohydrochloride" =

$$\left.\begin{matrix} NH_2{\cdot}Cl \\ | \\ NH_2 \end{matrix}\right\} = AH_3N,Cl.$$

As hydrazine salts these are perfectly normal, but it is a great mistake to regard the two first as mono- and dihydro-compounds; one is an oxyhydrate precisely as the other is a chlorhydrate; but any attempt by halving to make them "amidogen" compounds is quite impracticable. What then does Mr. Fischer say to this intruder on his domain?

Wokingham Road, Reading.

ON THE

WAVE-LENGTH OF THE PRINCIPAL LINE IN THE SPECTRUM OF THE AURORA.*

By WILLIAM HUGGINS, D.C.L. LL.D., F.R.S.

NOTWITHSTANDING the large number of determinations by different observers, since Angström in 1867, of the wave-length of the principal (and frequently the only) line in the spectrum of the Aurora, this value has not yet been accepted as definitely fixed with the degree of accuracy which is required for a final inquiry into its chemical origin. The uncertainty within rather wide limits, which seems still to obtain, has arisen mainly from the circumstance that in nearly all cases the observations have been made with a small direct-vision spectroscope, and under conditions which do not admit of an accurate determination of the value sought for. About half the number of some twenty-four observers agree pretty well, but among the results given by the others the differences are very large in relation to the accuracy which is required, though they are not greater, perhaps, than was to be expected from the circumstances under which the observations were made.

I think it is very desirable, therefore, that I should put on record some observations of the spectrum of the Aurora which I made in the year 1874, but which up to the present time have remained unpublished. These observations were made with a powerful spectroscope, and under conditions which enabled me to determine the wave-length of the principal line within narrow limits of error. The spectroscope was made by Sir Howard Grubb on the automatic principle of his father, Mr. Thomas Grubb. It is furnished with two "Grubb" compound prisms; each has 5 square inches of base, and gives about twice the dispersion of a single prism of 60°.

The object-glasses of the collimator and telescope are 1·25 inch in diameter. The definition is very good. Though the automatic arrangement works well, I always take the precaution to measure only small differences of position of the line to be determined from lines near it, the wave-lengths of which are known.

The observations were made on February 4, 1874. There was a brilliant Aurora, showing a whitish light; a direct-vision spectroscope resolved this light into a brilliant line in the yellow and a faint continuous spectrum.

The "Grubb" spectroscope was directed from the window of the observatory upon the brightest part of the Aurora. In the first instance an estimation by eye was made of the position of the bright line by comparing it in the instrument with the spectrum of a spirit lamp. The bright line was seen to fall on the more refrangible side of the line, for which Watts gives the wave-length 5582,† Angström and Thalén 5583†, by from one-fifth to one-fourth of the distance of this line from the beginning of the band. If we take one-fourth, we have λ5569·6; one-fifth gives λ5572·3. The mean of these values gives for the—

Aurora line λ5570·9 . . . . (1).

The cross-wires of the spectroscope were then brought upon the line, and the reading 3476 showed the line to fall about midway between two strong lines in the spectrum of tin, λ5564 and λ5587 respectively, according to my measures.‡ The position of the cross was then compared directly with those lines in the spectrum of an induction spark taken between electrodes of tin. The further details of this comparison are not given in my note-book, but the result only, which placed the—

Aurora line at λ5571 . . . . (2).

Consulting my map of the chemical elements, I found that there was a line of tellurium very near this place, namely, at λ5575; I therefore brought the spark from tellurium before the slit, when the cross appeared on the more refrangible side of the tellurium line. The measure of the distance of the cross from this line came out equal to λ0003. The place given in my paper for this line of tellurium is 5575. Thalén gives for the same line 5574·1.§ If we take the mean of these values and deduct 0003, we get for—

The line of the Aurora λ5571·5 . . . . (3).

There are strong lines of iron very near this position in the spectrum, and I made use of these also for a further determination of the place of the Aurora line. The cross, after having been placed upon the line of the Aurora, was confronted with these lines in the spectrum of iron.

The condensed account in my note-book does not give further particulars of this comparison, but states only that the place of the—

Aurora line came out λ5571·5 . . . . (4).

Summing up these determinations we have—

(1). Eye-estimation	λ5570·9
(2). From tin	5571·0
(3). From tellurium	5571·5
(4). From iron..	5571·5

* A Paper read before the Royal Society, March 7th, 1889.

* *Phil. Mag.*, vol. xli., 1871, p. 14.

† "Spectres des Métalloides," *Nov. Act. Upsal. Scs.*, ser. 3, vol. ix., p. 29.

‡ "Spectra of the Chemical Elements," *Phil. Trans.*, 1864, p. 139.

§ *Brit. Assoc. Rep.*, 1885, p. 292.

From these values I think that we are justified in taking for the Aurora line, as a position very near the truth,—

$$\lambda 5571 \pm 0{\cdot}5 \quad . \quad . \quad . \quad . \quad (5).$$

Among the numerous determinations of other observers, those of Professor H. C. Vogel in 1872* seem to me to have great weight. A direct-vision spectroscope with a set of five prisms was used. The reduction of the readings of the micrometer into wave-lengths was based upon the repeated measures of 100 lines of the solar spectrum.

The screw had been thoroughly examined. After each observation of the Aurora lines, readings were taken of the lines of sodium or of hydrogen. The observations extended over four nights. On three nights four separate readings were obtained; on the fourth night two only. Vogel gives as the mean result of the fourteen observations—

$$\text{Aurora line } \lambda 5571{\cdot}3 \pm 0{\cdot}92 \quad . \quad . \quad . \quad . \quad (6).$$

Perhaps I should state that I find from a remark in my note-book that at the time of my observations in 1874 I was not aware of Vogel's results, and I could not, therefore, have been biassed in any way by them.

The recent observations on the spectrum of the Aurora by Gyllenskiöld at Cap Thordsen in 1882, deserve special mention.† With a Hoffmann spectroscope, furnished with a scale, he obtained at Cap Thordsen in 1882 a mean result of $\lambda 5568 \pm 1{\cdot}6$. Later, in 1884, at Upsala, with a Wrede spectroscope furnished with a micrometer screw, a mean value for the Aurora line, $\lambda 5569 \pm 6{\cdot}2$.‡ Gyllenskiöld discusses in detail nearly all the recorded observations of the spectrum of the Aurora from 1867 to 1882, and then brings them together in a table with such probable errors as the original statements of the observers enabled him to assign to them. I think it is desirable to give that part of his list which contains the observations of the brightest line:—

1867.	Angström	Upsala	λ5567 ±	1·0
1868.	Struve	Poulkowa	5552	14·9
	Lemström	Tromsœ	5659	14·0
1869.	Peirce	Etats Unis ..	5565	10·8
1870.	Proctor	.. ..	5995	25·0
1871.	Smyth	Edinburgh ..	5579	9·5
	Lindsay	Aberdeen	5680	50·0
	Barker	New Haven ..	5594	13·0
1872.	Vogel	Kiel	5571	0·9
	Denza	Moncalieri ..	5568	11·9
	Donati	Florence	5569	10·0
	Oettingen	Dorpat	5548	30·0
	Respighi	Rome	5574	10·0
	Wijkander	Spitzberg	5572	1·0
1873.	Backhouse	Sunderland ..	5660	10·0
	Barker	New Haven ..	5569	13·9
	Lemström	Enare	5569	0·5
1874.	Backhouse	Sunderland ..	5570	10·0
	Maclear	"Challenger" .	5522	37·1
1879.	Nordskiöld	Pitekaie	5563	10·0
1880.	Copeland	Dunecht	5572	2·0
1882.	Gyllenskiöld . ..	Cap Thordsen .	5568	1·6
1884.	„ . ..	Upsala	5569	6·2

Gyllenskiöld then calculates by the method of least squares the mean value of all the determinations, and finds the following result§:—

Mean value of the 23 observations, $\lambda 5570{\cdot}0 \pm 0{\cdot}88$. (7).

The recent measures by C. C. Krafft‖ depart largely from Gyllenskiöld's mean value. Krafft found on—

1882, November	2	λ5595
„	„ 11	5586

and measures with the same instrument, made by Schroeter on November 17th, gave λ5587.

Now, though Angstrom's original value λ5567 may not be quite accurate, his observation fixed a limit towards the red, beyond which the Aurora line cannot lie. Angstrom says, "sa lumière était presque monochromatique et consistait d'une seule raie brillante située à gauche" (on the more refrangible side) "du groupe connu des raies du calcium."* The position of the most refrangible line of this calcium group is accurately known; according to†

Kirchhoff	λ5580·9
Thalén	5580·9
Huggins	5581·0

It is certain, therefore, from Angstrom's first observation in 1867 alone, that the Aurora line lies well on the more refrangible side of wave-length 5580. This limit towards the red was confirmed afterwards by Angstrom himself; he says later that the yellow line falls almost midway between the second and third line of the shaded carbon group.‡ The positions of these lines of comparison are, according to Angström and Thalén, λ5538 and λ5583.§

It follows that Krafft's values, λ5586, λ5587, and λ5595, must be from some cause inaccurate. A possible explanation may be found in the small number of solar lines employed by Krafft for the reduction of the measures into wave-lengths. The curve was drawn through the six Fraunhofer lines B, C, *a*, D, E, and *b*. There was no control for the curve between D and E, and a very small deviation of the curve from its true position here would be sufficient to account for the position of less refrangibility of from λ0016 to λ0024, which his measures give for the Aurora line.

It should be stated that Krafft exp,esses regret that more attention could not be given to the spectroscopic observations. He says:—"Leider gestatteten die obligatorischen Beobachtungen nicht, den spectroscopischen Untersuchungen die gehörige Aufmerksamkeit angedeihen zu lassen . . . . Ich glaubte ausserdem diese Messungen um so mehr auslassen zu können, als der Platz der gewöhnlichen Nordlichtlinie oft und sehr genau bestimmt ist."

To sum up, we have the following values for the principal line of the Aurora:—

(6).	1872, Vogel	λ5571·3 ±	0·92
(5).	1874, Huggins	5571·0	0·5
(7).	Gyllenskiöld's mean of 23 observers from 1867 to 1884	5570·0	0·88

These values agree closely, and fix within very narrow limits the position in the spectrum, where we have to seek the chemical origin of the line.

Gyllenskiöld, from his observations of the changes which occur in the spectrum of the Aurora, comes to the conclusion that: "le spectre de l'Aurore boréale résulte de la superposition de plusieurs spectres différents," and that "la raie principale forme un de ces spectres élémentaires; elle apparait très souvent seule." A similar view was taken many years ago by Angström¶ and by Vogel.¶

[After consideration I think that I ought to point out that Mr. Lockyer's recent statement** that:—"The characteristic line of the aurora is the remnant of the brightest manganese fluting at 558," is clearly inadmissible, considering the evidence we have of the position of this line.

* *Leipzig Math. Phys. Berichte*., vol. xxii., p. 285.
† *Observations faites au Cap Thordsen, Spitzberg, par l'Expédition Suédoise*, vol. ii., p. 1; Aurora Borealis, par Carlheim Gyllenskiöld, Stockholm, 1886.
‡ *Ibid*., p. 166.
§ *Ibid*., p. 169.
‖ "Boebachtung-Ergebnisse der Norwegischen Polarstation," &c. A. S. Steen. Christiania, 1888.

* *Spectre Solaire*, Upsal, 1868, p. 42.
† *Brit. Assoc. Rep*., 1884, p. 372.
‡ *Nature*, vol. x., p. 211.
§ *Acta Upsal*., ser. 3, vol. ix., p. 29.
‖ *Nature*, vol. x., p. 210.
¶ *Leipzig Math. Phys. Berichte*, vol. 23, p. 298.
** *Roy. Soc. Proc*., vol. xlv. (1889), p. 234.

In support of this statement Mr. Lockyer says:—Angström gave the wave-length of the line as 5567, and since then many observers have given the same wave-length for it, but probably without making independent determinations. Piazzi Smyth, however, gives it as 558, which agrees exactly with the bright edge of the manganese fluting. R. H. Proctor also gives the line as a little less refrangible than Angström's determination. He says:—'My own measures give me a wave-length very slightly greater than those of Winlock and Angström'" (*Nature*, vol. iii., p. 468).

By reference to Gyllenskiöld's table it will be seen that the probable errors of the determination by Piazzi Smyth and Proctor, $5579 \pm 9{\cdot}5$ and $5595 \pm 25{\cdot}0$ respectively,* are too large to entitle these measures to special weight.

Mr. Lockyer says further:—"Gyllenskiöld's measures with the Wrede spectroscope also give 5580 as the wave-length of the characteristic line. I feel justified, therefore, in disregarding the difference between the wave-length of the edge of the manganese fluting and the generally accepted wave-length of the Aurora line."

Gyllenskiöld's single measure of 5580, on which Mr. Lockyer relies, differs widely from the values which Gyllenskiöld himself assigns to this line, namely, from observations at Cape Thordsen in 1882, $\lambda 5568 \pm 1{\cdot}6$, and from observations at Upsala in 1884 with the Wrede spectroscope, $\lambda 5569 \pm 6{\cdot}2$.

Speaking of Krafft's observations, Mr. Lockyer says†:—"The wave-lengths obtained for the Aurora line were 5595, 5586, and 5587. Unlike most observations, these place the Aurora line on the less refrangible side of the manganese fluting. Hence we have an additional reason for neglecting the difference between the wave-length of the brightest edge of the manganese fluting and the commonly accepted wave-length of the Aurora line, as given by Angström. . . . . These observations are the latest which have been published, and were obviously made with a full knowledge of all previous work, so that their importance must be strongly insisted upon."

I have already pointed out that Krafft's measures were not made under circumstances which assured to them a high degree of accuracy; and Krafft's own words, which I have quoted, disclaim expressly any special attempt on his part to re-determine the position of the principal line with a higher degree of accuracy than the observers who preceded him.—March 4].

ANALYSES OF WATERS OF THE YELLOWSTONE NATIONAL PARK,

With an Account of the Methods of Analysis Employed.‡

By FRANK AUSTIN GOOCH and JAMES EDWARD WHITFIELD.

(Concluded from p. 156).

Treatment of the Aqueous Solution.

The aqueous solution, its degree of concentration having been determined in the manner already described, was divided into five portions. Two of these were taken for the determination of bromine, iodine, lithium, cæsium, rubidium, and thallium, in duplicate; two for the determination in duplicate of arsenic, antimony, tin, copper, lead, and boron; and the remaining portion was reserved to be used in an emergency.

Iodine and Bromine.—The portion for the determination of the elements of the former group was weighed and evaporated to a pasty condition. The residue was thoroughly extracted with strong alcohol, treated with water, reduced again nearly to dryness, and again extracted with alcohol. The extract was evaporated after the addition of a drop or two of a strong solution of sodium hydrate, and this residue was extracted with alcohol like the former residue. The residues of the extractions with alcohol were kept for subsequent treatment. The alcoholic solution containing presumably all the iodine and bromine, with a small proportion of the chlorine originally in the water, was evaporated to dryness, and the solution of the residue in water was acidulated with sulphuric acid mixed with a solution of ferric sulphate introduced into a retort of the pattern previously described and figured in connection with the determination of boric acid in the natural waters, and distilled. The distillate was collected in a U-tube attached to the condensing tube and sealed with carbon disulphide and water. If iodides are present in the retort to the minutest degree the iodine is set free as such, its characteristic colour appears in the seal of carbon disulphide, and its amount may be determined by titration in the usual manner with sodium hyposulphite.

In the waters which we examined iodine was not present in sufficient quantity to appear in the test of the amounts at our disposal.

To the liquid remaining in the retort after the distillation had been prolonged sufficiently to ensure the complete volatilisation of the iodine a few crystals of potassium permanganate were added, and the distillation was continued. This distillate was collected as before in a U-tube joined to the condenser, but the seal was made with chloroform and water. At the beginning of the operation the seal of the U-tube showed in most cases the characteristic colour of bromine, but this was discharged before the end of the operation by the excess of chlorine and replaced by the colour of the latter. The contents of the U-tube were transferred to a beaker and treated with pure sodium hydrate and zinc, and from the solution of sodium bromide and chloride thus obtained the silver salts were precipitated by silver nitrate, in the usual manner, after acidifying with nitric acid. The silver bromide and chloride thus precipitated were collected together upon asbestos in a perforated crucible, dried, weighed, and dissolved in potassium cyanide. From the cyanide solution the silver was deposited by electrolysis, according to the process described elsewhere by one of us for the indirect estimation of bromine in the presence of chlorine.* In this manner we obtained the weight of the mixture of silver chloride and silver bromide, and the weight of the silver contained in the mixture. The amounts of bromine and chlorine in the mixed salts were determined from these data by the solution of a simple algebraical equation.

Lithium.—The contents of the retort after the distillation of the bromine were united with the residues of the extractions by alcohol, the excess of sulphuric acid was volatilised, the residue dissolved in hydrochloric acid, the sulphates converted to chlorides by means of barium chloride, the baric sulphate thus formed separated by filtration, alumina, silica, and barium carbonate precipitated by ammonium carbonate and separated by filtration, and the solution evaporated to dryness. The residue was gently ignited to remove ammonium chloride, dissolved in water acidulated with hydrochloric acid, and this solution, concentrated until just ready to deposit, was drenched with strong alcohol. The sodium chloride precipitated was washed with alcohol until the spectroscope indicated entire freedom from lithium chloride. The alcoholic solution of lithium chloride was evaporated to dryness, and the residue was dissolved in a little water acidulated with hydrochloric acid. This solution was treated with a little pure barium hydrate (made from the nitrate precipitated from nitric acid) to remove traces of magnesia, and filtered, and from the filtrate the barium was removed by treatment with ammonium carbonate,

* Gyllenskiöld's statement of Proctor's value is based on *Nature*, vol. iii., p. 347 and p. 68.

† *Roy. Soc. Proc.*, vol. xlv. (1889), p. 241.

‡ *Bulletin of the United States Geological Survey*, No. 47.

* *Bulletin of the U.S. Geological Survey*, No. 42, p. 80; *Am. Chem. Jour.*, vol. viii., p. 421

repeated if necessary. From the solution of lithium chloride thus obtained the lithium was separated according to Mayer's method* by evaporation with hydro-disodic phosphate and sodium hydrate, the treatment of the residue with sufficient hot water to dissolve the salts, which should be soluble with the aid of gentle heat, the addition of an equal volume of ammonia, and digestion in the cold during twelve hours. The precipitate was filtered upon asbestos in a perforated crucible, washed with a mixture of equal parts of ammonia and water, ignited, and weighed. The filtrate from this precipitate was evaporated, and the residue of evaporation again treated as before to recover traces of lithium; and a similar process of treatment was applied to the filtrate from the second precipitate. The three precipitates thus obtained contained presumably all the lithium as the tribasic phosphate.

This is the method of determining lithium which was employed previous to the development of the process which has been described in connection with the account of the determination of lithium in the natural waters (*see ante*). Were the work to be repeated we should unquestionably employ the amyl alcohol process exclusively, although it may be said for the determinations by Mayer's method that their actual error was very much diminished by the use of comparatively larger portions of material for the analysis, and we are confident that the results are, on that account, fairly trustworthy.

Cæsium, Rubidium, and Thallium.—The filtrate from lithium phosphate was freed from ammonia by boiling; the phosphoric acid was precipitated by ferric chloride and ammonia, with the usual precautions to secure a suitable proportion of the iron salt and to keep the excess of ammonia at the lowest possible limit, and removed by filtration; the filtrate from ferric phosphate and ferric hydrate was evaporated to dryness and gently ignited to remove ammonium salts; the residue thus left was dissolved in water and treated with platinic chloride in excess of the amount necessary to convert all the alkaline chlorides present to platinum salts.

The precipitate by platinic chloride was extracted by boiling repeatedly with small portions of water, and the residues of this treatment were tested from time to time spectroscopically. The characteristic lines of cæsium and rubidium appeared more distinctly toward the end of the process of extraction when they were visible at all. Thallium, which should appear, if present, in the intermediate extracts, failed to show itself in any of the waters.

Arsenic, Antimony, Tin, Copper, and Lead.—The weighed portion of the concentrated solution was acidified with hydrochloric acid, heated to 70° C., and submitted to the action of a current of hydrogen sulphide during several hours. The precipitated sulphide was filtered off upon anthracene in a perforated crucible, following the method described by one of us.† The crucible with the adherent filter of anthracene and the precipitate were placed in a small beaker, drenched with benzol, and gently warmed until the anthracene dissolved. Water containing sodium hydrate was added and, after sufficient digestion on the water-bath, the liquid and precipitate were transferred to a paper filter, previously moistened with water. In this manner the aqueous solution, carrying the arsenic, antimony, and tin, if present, was permitted to traverse the filter, while the sulphides of copper and lead, with possibly free sulphur, remained with the benzol upon the filter. After thorough washing with water the receptacle for the filtrate was changed, the filter was moistened with alcohol, and thus the benzol, with the anthracene in solution, was induced to pass through the paper, which, with the residue upon it, was washed with benzol followed by alcohol and then by water. The filter was carefully insinerated, and the ash was digested with a few drops of nitric acid. The solution thus obtained was evaporated to dryness, the residue was moistened with hydrochloric acid, and, after the volatilisation of the most of the acid, dissolved in hot water. From this solution hydrogen sulphide should precipitate copper and lead as sulphides. In the single case of that water which had been concentrated in porcelain no black sulphide was obtained at this point in the operation; in other cases, a trifling black precipitate fell, which subsequent examination proved to be copper sulphide exclusively, doubtless originating in the concentrating vessel.

The second precipitation with hydrogen sulphide was introduced to test the presence of copper and lead, in the process just outlined, because the residue left upon the filter when the benzol is washed from it is apt to be dark in colour, even in the absence of black sulphides.

The alkaline filtrate from the benzol and the insoluble residue were acidified with hydrochloric acid, after the addition of a drop or two of ammonium sulphide; the precipitate was filtered off on asbestos in a perforated crucible; the filter and precipitate were dried and treated in a small beaker with fuming nitric acid; the solution in nitric acid was evaporated to dryness, the residue was dissolved in hydrochloric acid, and from this solution, made strongly alkaline with ammonia containing some ammonium sulphide (the last to keep tin, if present, in solution), but kept small in volume, the arsenic was precipitated by the magnesium chloride mixture. The liquid was briskly stirred and then allowed to stand quietly for twelve hours at least. The precipitate was transferred by means of the mother liquor, without the use of other liquid, to a perforated crucible carrying an asbestos felt, washed with a mixture of one part of ammonia to three of water, dried carefully, ignited in an atmosphere of oxygen, and weighed as magnesium pyroarsenate.

The filtrate from the ammonio-magnesium arsenate, which should contain the antimony and tin of the water, was evaporated to remove the great excess of the ammonia, and acidified with hydrochloric acid. The sulphur thus precipitated should carry with it the antimony and tin as sulphides, In no case were we able to detect antimony in this precipitate. In one or two cases there were evidences of the presence of tin, but this doubtless came from the lining of the vessel in which concentration was effected; in the water which was concentrated in porcelain no tin was found.

Boric Acid.—The filtrate from the original precipitate by hydrogen sulphide in the acid solution was warmed gently, submitted to the action of a current of air to blow out the excess of hydrogen sulphide, brought nearly to neutrality by the addition of sodium carbonate, made faintly alkaline with ammonia, filtered from the precipitate thus thrown down, and evaporated nearly to dryness after the addition of enough sodium hydrate to expel the ammonia and yet preserve strong alkalinity. The residue was acidified with hydrochloric acid and extracted thoroughly with alcohol, and the alcoholic solution was made alkaline with sodium hydrate and evaporated to dryness. This residue was dissolved in water, just acidified with hydrochloric acid, and from the solution the last traces of silica, alumina, lime, and phosphoric acid were removed by the action of ammonia and ammonium carbonate, and filtration. In the filtrate the boric acid was determined according to Marignac's process, by treatment with magnesium chloride, ammonium chloride, and ammonia, evaporation to dryness, ignition at a red heat, extraction with boiling water, and the repetition upon the extract of the process of evaporation, ignition, and extraction. The residues left after extraction were together ignited and weighed, and the magnesia in the weighed material was determined by precipitation as the ammonio-magnesium phosphate and weighing as the pyrophosphate. The difference between the weight of the residue and its contents in magnesia is boric acid.

This was the process which we employed in the earlier determinations. The process which was developed later,

* Fresenius's "Quant. Anal.," 6th Aufl., Band II., p. 215.
† *Bulletin of the U.S. Geological Survey*, No. 42, p. 86; *Am. Chem. Journ.*, vol. vii., 1885—86, p. 87.

and applied to the determination of boric acid in the natural waters, is preferable.

Statement of the Results of Analysis.

In stating the facts deduced from the analysis of the waters, it has seemed best to adopt the plan of recording the oxygen acids as anhydrides, the basic elements as such, and the oxygen which must exist in combination with the bases by itself; thus avoiding an arbitrary division of the basic elements among the oxygen acids and halogens. The basic oxgen, so-called, of the alkaline waters was found by computing the amount of oxygen which would exist in the oxides of the basic elements and deducting from this amount the weight of oxygen equivalent to the halogen discovered by analysis. In the case of waters which carried such an excess of acid that the halogens may be supposed to be uncombined with bases, the basic oxygen is the amount of oxygen which would exist in the oxides of the basic elements. In waters of such acidity that a portion only of the halogen may be supposed to be in combination with basic elements the equivalent in oxygen of the amount of halogen which is regarded as in combination was deducted from the total amount of oxygen of the oxides in computing the basic oxygen. The halogen which remains uncombined with the basic elements was, as a matter of course, assumed to be in association with hydrogen.

The hypothetical combination of the elements found in the waters must necessarily be largely imaginary, for nothing is more plainly evident than the impossibility of stating authoritatively, in the present condition of knowledge, the actual division of a number of acids among a number of bases in solution. This we do know, that the combination is determined not only by the relative proportions of all the constituents, but by the absolute quantities of all associated in a definite amount of liquid. It is with no purpose, therefore, of attempting to represent actual conditions of combination, but only for the sake of securing a common ground of comparison among themselves and with other waters, that we have assumed arbitrarily the existence in these waters of the definite and simple combinations of the following scheme :—

In alkaline waters, bromine has been combined as KBr; B_2O_3 as $Na_2B_4O_7$; As_2O_5 as $NaAsO_2$; P_2O_5 as Na_2HPO_4; chlorine has been assigned to the bases in the order NH_4, Li, K, Na; SO_3 has been linked with such bases as remain in the order NH_4, Li, K, Na, Mg, Ca; residual bases have been classed as neutral carbonates in the order Mg, Ca, Na; residual sodium has been represented as $NaSiO_3$; aluminum and iron have been put down as Al_2O_3 and Fe_2O_3; and residual CO_2 and SiO_2 have been shown as such.

In making up the hypothetical composition of acid waters the same general arrangement has been kept as far as possible in order to secure ready comparison with the alkaline waters. Though the relative avidity of hydrochloric acid is greater at ordinary temperatures than that of sulphuric acid, we have nevertheless represented hydrochloric acid as the free acid whenever it became necessary to represent one of them as free.

The sulphuric acid indicated by the analysis has been combined with the bases in the order Ca, Mg, Al_2, Fe_2, Na, K, Li, NH_4; the residual bases have been combined with chlorine in the same order; the anhydrides B_2O_3, As_2O_3, P_2O_5, SiO_2, CO_2, and residual SO_3, have been stated as such; residual chlorine has been represented as HCl, and H_2S as such.

It is apparent that in some instances combinations have been imagined which might exist under some of the circumstances encountered, but which are improbable under other conditions met with in waters of a generally similar character; thus, for the sake of uniformity, we have represented the boric acid of the alkaline waters invariably as $Na_2B_4O_7$, and the phosphoric acid as Na_2HPO_4, regardless of the variable action of an excess of alkaline carbonate upon these salts in hot solutions and under prolonged digestion. So, also SiO_2 has been stated as free, when, if so, it must have been in solution in the presence of the carbonates of sodium, magnesium, and calcium; the neutral carbonates have been represented as such in the presence of free carbonic acid, both in hot and in cold waters; and potassium has been arbitrarily associated with bromine; and ammonium, lithium, and potassium have been preferred to other bases in combining the chlorine.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 23, 1889.

Prof. Reinold, F.R.S., President, in the chair.

The following gentlemen were elected members:—Sir James M. Douglas, Sir Douglas Galton, Messrs. C. W. Biggs, C. Capito, A. C. Cockburn, R. E. Crompton, J. M. Gorham, C. G. Gümpel, W. H. Massey, E. Moynihan, F. J. Mudford, R. W. Paul, and C. E. Spagnoletti.

Prof. J. V. Jones read "*Notes on the Use of Lissajou's Figures to Determine a Rate of Rotation, and of a Morse Receiver to Measure the Periodic Time of a Reed or Tuning-fork.*"

In determining resistance absolutely by the B.A. or by Lorenz's method it is important to know the speed of rotation at the instant when the deflection of the galvanometer needle is observed. To determine this, an arm carrying a mirror is caused to oscillate by a pin placed eccentrically in the end of the spindle, and a Lissajou's figure is obtained by using another mirror mounted on a vibrating reed driven electrically. Equality of period is obtained when the resulting elliptical figure is permanent, and the frequency of the reed is determined subsequently. In making the experiments it is found convenient to control the speed of the disc by braking it either with the finger or a piece of wood. The reed consists of a rectangular steel rod 100 c.m. long and section $1{\cdot}51 \times 0{\cdot}60$ c.m., and the length of the vibrating segment can be altered by sliding it through a clamp. To permit of this change without altering the electrical contacts, the latter are formed by two independent springs, one of which is always in contact with the rod. For determining the frequency of the reed a second pair of contacts are operated by the vibrator, and the currents recorded by a Morse receiver, whilst simultaneously the paper receives marks from a pen controlled by a standard clock. The limit of accuracy of this part of the experiment is found to be 1-10th per cent, due to changes in the reed's frequency. This is a serious defect, and the author of the paper asked for advice as to the precautions necessary to obtain reeds of constant pitch.

Prof. Ayrton, whilst recognising the extreme importance of determining speed accurately, suggested that the inconstancy of the reed may be due to the impulse being given at the end instead of at the middle of its swing, and recalled an experiment shown before the Society by Prof. Perry and himself, in which the pitch of an electrically driven fork was varied greatly by altering the adjustment of the contact-screw. Referring to Dr. Thompson's modification where two tuning-forks drive each other, it was pointed out that the method requires the synchronism of the two forks to be very exact.

Mr. Blaikley enquired whether any doors were opened or closed during the experiments, as the pitch of a reed is affected by the size of its resonance chamber. He also stated that the pitch of reeds driven pneumatically could be maintained constant to 1 part in 10,000, and mentioned that two forks nearly in unison influence each other's period when near together.

Referring to the two forks mentioned by Prof. Ayrton, Prof. S. P. Thompson said it was advantageous to mount such forks on sounding-boxes, for, when placed at a suitable distance apart, they then exert considerable mutual control.

The sketch put on the board by Prof. Jones led Dr. Thompson to suppose that a perfect method of driving forks had been devised, for two springs were shown touching opposite sides of the box, and such an arrangement might be used to complete the circuit only when the reed is in the middle position. He also believed that forks give greater constancy than single reeds, and mentioned some recent improvements in which one prong of an electrically driven fork is made of phosphor bronze.

Mr. T. H. Blakesley, reasoning from ideas suggested by Mr. Strob's experiments on vibrating membranes, concluded that the periods of forks placed ¼ wave-length apart would not uninfluence each other.

In reply to a question from Mr. F. J. Smith, Prof. Jones thought there could be no "creeping" of the reed through the clamp. He also stated that he had been led to use a reed from the results obtained in Delaney's system of telegraphy, and the fact that Lord Rayleigh considered electrically driven forks satisfactory.

Dr. Hopford read extracts from the following papers:—

"*On the Clark Cell as a Source of Standard Currents.*" By Prof. R. Threlfall and Mr. A. Pollock.

The authors find, contrary to ordinary ideas, that Clark cells can be used to send currents of considerable magnitude without the E.M.F. being appreciably changed, and have constructed cells which give 0·001 ampere steadily for half an hour. This result has been obtained by increasing the size of the cell, so that each electrode is about five square inches in area and the internal resistance is about six ohms. For the ordinary small test-tube cell, the resistance of which may be about 1500 ohms, the current ought not to exceed 0·00001. On closing the circuit the P.D. (potential difference) drops almost instantaneously to its steady value, and, when the circuit is opened rises equally rapidly to very nearly the original E.M.F. The cells completely recover in time. If the current sent be too large the P.D. falls for a time, and afterwards rises and tends towards a fixed value. In this respect Clark's cells are greatly superior to large Daniell's sending current through the same resistance. The paper contains several tables and curves, as well as valuable results respecting the close agreement between the E.M.F. of a great number of different cells.

"*On the Application of a Clark's Cell to the Construction of a Standard Galvanometer.*" By Prof. R. Threlfall.

A large cell as above mentioned, together with a known platinoid resistance, are used to standardise a reflecting galvanometer, constructed with a single movable coil, sliding in guides so as to vary the constant in known proportions. Two controlling magnets are carried on opposite sides of a sleeve sliding on a central tube enclosing the long fibre, and a small hollow copper cylinder in oil acts as a damper. The tangent law was found by calculation to be practically correct up to 15°, and the scale is curved so as to read tangents on a scale of equal divisions. To give this result the approximate polar equation to the curve is shown to be $r=f(1+0{\cdot}207\,\theta^2+0{\cdot}0269\,\theta^4)$. In standardising the instrument a known current is sent through it from the Clark cell, and the controlling magnets adjusted till the spot comes to a fiducial mark on the scale. By varying the position of the coil currents ranging from 0·001 to 0·4 ampere can be measured.

"*On the Measurement of High Specific Resistances.*" By Prof. Threlfall.

The chief points dealt with are the means for producing thin plates of material of known dimensions, the form and methods of magnetising the needles, and the arrangement of suspension found necessary when great sensibility is required. For producing the plates two plane platinised brass slabs are used and kept at a known distance apart by micrometer screws, whilst the material is melted between them. The screws are then withdrawn and the resistance determined by comparison with a megohm, using different E.M.F.'s in the two cases, so as to obtain about equal deflections. As regards the galvanometer, after many unsatisfactory attempts to use one made according to the Messrs. Gray's pattern, the coils of that instrument were mounted in the ordinary way, and used with an astatic combination of magnetised steel discs. Extreme care was taken to obtain discs exactly similar, and a pair of electro-magnets were made to magnetise them *in situ*, so as to obtain great astaticism. For suspending the magnets quartz fibres were found greatly superior to silk, the zero of the instrument being very indefinite, even with a silk fibre thirty inches long. Considerable difficulty was experienced in attaching the mirror to the needle on account of the distortion produced by ordinary elements; slow drying white paint was ultimately used and found satisfactory.

"*On the Measurement of the Resistance of Imperfectly-purified Sulphur.*" By Prof. Threlfall and Mr. A. Pollock.

The apparatus used is described in the previous paper, the galvanometer of 16000 ohms being arranged to give 1 division for 2×10^{-12} amp. A mean of the results obtained gives about 11×10^{18} ohms per c.c. as the specific resistance. In performing the experiments many precautions were required to prevent air currents and magnetic disturbances, and paraffin keys were found to give much better insulation than ebonite ones. In conclusion the authors enumerate the chief points to which attention should be paid in designing and using very sensitive galvanometers. They consider it desirable to use quartz fibres at least six feet long, to provide very fine adjustment for the controlling magnets, whose supports should be independent of the suspension arrangement, and believe the whole should be placed in a thick soft iron cylinder.

Mr. Boys, speaking of attaching mirrors to wires, said he found a very small speck of shellac varnish to be very satisfactory. As regards quartz fibres, Prof. Threlfall's method of producing them differed materially from his, and the fibres were much thicker. He considered it quite unnecessary to use fibres anything like six feet long, and thought fifteen inches quite sufficient where the weight to be supported was not large.

Prof. Ayrton regarded the results obtained from Clark's cells to be of extreme scientific and commercial importance, for they showed that a very convenient standard of E.M.F. could also be used as a standard for current.

Prof. Thompson, after commenting on the convenience of good E.M.F. standards, expressed a hope that Prof. Threlfall would be able to suggest a convenient method for producing a standard ampère.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, April 1, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Septimus Felix Beevor, B.A.; Professor J. A. Fleming, M.A., D.Sc.; John Langston, J.P., F.R.C.S.; and Major S. Flood Page.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

Appointment. — Mr. Charles H. Piesse, A.K.C. (Lond.), M.R.C.S., F.I.C., &c., of Cassiobury House, Fulham, and New Bond Street, has been appointed Consul-General in London for the Principality of Monaco.

NOTICES OF BOOKS.

Exercises in the Preparation of Organic Compounds. By Professor EMIL FISCHER, of Würzburg. Translated with Permission of the Author from the Second German Edition by ARCHIBALD KLING, F.I.C., Chief Assistant, Chemical Laboratory, Glasgow and West of Scotland Technical College. With a Preface by W. DITTMAR, LL.D., F.R.SS.L. and E., Professor of Chemistry in the Glasgow and West of Scotland Technical College. Glasgow: W. Hodge and Co. London and Edinburgh: Williams and Norgate.

TEACHERS of chemistry and students who aim at acquiring a sound knowledge of the organic department of the science will find this little work exceedingly useful. They will find here instructions which have been verified during long and extended practice in the laboratories of the Universities of Erlangen and Würzburg. It will be perceived that the substances whose preparation is here described have not been taken at random, but have been selected so as to illustrate the principal operations and the most important methods which are brought into requisition in organic chemistry. It is not too much to say that the student who has worked carefully and intelligently through the operations described in this book will have taken a considerable step towards qualifying himself for original research or for taking part in the industrial preparation of organic compounds.

We have been much pleased with a remark made by Professor Dittmar in his "Introductory Preface." He writes:—"The present book, as a comparison will show, is a close translation of the original; I don't believe in 'adaptations'; if a book is worth translating, translate it as it stands." The writer here lays his finger upon a real evil. We know foreign works which, in the course of translation, have been by no means improved by "adaptation" to British educational prejudices.

Whilst we can conscientiously recommend this book we must admit that it is written for the genuine student, not for the intending examinee. It will surely aid the former to "know," but it will scarcely help the latter to "pass."

**The Proprietor Face to Face with his Forsaken Farm.* Lectures delivered at Brussels at the Request of the Central Society of Agriculture. By M. GEORGES VILLE.

†*M. Georges Ville and Agricultural Belgium.* Lectures delivered at Brussels during the Year 1874 at the Request of the Central Society of Agriculture. By M. GEORGES VILLE. Paris: G. Masson.

UNLIKE too many chemists, physicists, and engineers of the present day, M. Ville is nobly seeking to increase the productiveness of the soil, so that the agriculturist of Europe, and especially of France, may not be crossed by the competition of America and India, the future of which he views with alarm. But he does not take into consideration a still more serious evil in the background. The time must come when the United States will require their total produce for the support of their own population. Similar will be the case ultimately with India, Australia, the La Plata Regions, &c. The country, then, which cannot grow food for its inhabitants will be in evil plight. But this consideration, far from invalidating the teachings of M. Ville greatly enhances their weight.

The author combats the old prejudice against chemical manures, and the superstition—we can give it no better name—that matter acquires a new value as plant-food by having been passed through the digestive organs of an animal. He does not, as some of his critics have asserted, reject farmyard manure as useless. When produced he would have it turned to full account. But he condemns as unscientific and uneconomical the keeping of stock for the purpose of producing manure. Even in these days we sometimes hear the farmer advised to buy not superphosphate, sulphate of ammonia, nor Bolivian nitre, but "some good feeding stuff!"

The only part in M. Ville's teachings concerning which doubt may be entertained is the great weight which he lays upon lime in the form of gypsum. In all his manurial formulæ, no matter for what crop or on what soil, this ingredient figures largely. Combined nitrogen, potash, superphosphate, and gypsum are his four principles, varying in proportion according to the kind of plant. This certainly seems strange if we reflect that most soils contain lime, often in considerable proportions, and that even the best superphosphates have rarely less than 50 per cent of calcium sulphate. His experiments, we must admit, show somewhat better results in the presence of gypsum then in its absence. But agricultural practice in England does not lead to corresponding results, and our experts generally pronounce gypsum in chemical manures a make-weight. We see that in the grain of cereals, in the seeds of the bean, and the tubers of the potato, *i.e.*, the portions which are most likely to be consumed away from the farm, the magnesia exceeds in the wheat, whilst in the straw, as well as in turnips, hay, and clover, that is to say, in the products which are generally returned to the soil, lime is in excess.

The two works before us may be characterised as forming a popular summary of M. Ville's more extensive treatise on "Artificial Manures," which already exists in an English version.

* "Le Proprietaire devant sa Ferme Délaissée."
† "M. Georges Ville et La Belgique Agricole."

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

SIR,—"X" refers me to papers in the *Journal of the Chemical Society*. These to me are inconclusive. Green vitriol was experimented upon a quarter of a century at least before Dr. Griffiths took it up, and he has not added anything to our knowledge regarding it. The late Dr. Voelcker proved that green vitriol was both plant food (indirectly) and plant poison (directly). It is strange that sulphate of ammonia has not gone down to 10s. per ton if we are to credit what "X" says in regard to what Professor Muntz says.—I am, &c.,

JOHN GEDDES MCINTOSH.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 11, March 18, 1889.

On the Fixation of Nitrogen during Slow Oxidations.—M. Berthelot.—If an old sample of ether, which has been preserved for months or years in bottles only partially full, is agitated with a small quantity of lime-water absolutely free from nitrates, and if this water is carefully evaporated to dryness, the residue, re-dissolved in a few drops of water and evaporated anew, yields, with strong sulphuric acid and ferrous sulphate, the red colour characteristic of nitric acid. It yields also the blue

colouration of diphenylamine, but this colour is not specific, and its use is open to errors which the physiologists have not sufficiently guarded themselves against. The blue is produced by a great number of oxidising bodies, including hydrogen peroxide.

The Formation-heat of Hydrogen Peroxide.—M. Berthelot and P. Petit.—This thermo-chemical paper does not admit of useful abstraction.

Preparation of Cuprous Chloride and Bromide by Means of the Alkaline Haloids and Copper Sulphate.—M. Denigès.—For the preparation of cuprous chloride the author heats to a boil in a flask one part each of crystalline copper sulphate and copper turnings, two parts sodium chloride, and ten parts of distilled water. The solution is filtered into 15 to 20 parts of water acidulated with 1 to 2 parts of acetic acid. If the hot liquid is collected separately after filtration and secluded from air it yields on cooling fine crystals of cuprous chloride. The same liquid dissolves carbon monoxide and hydrogen phosphide.

New and Characteristic Reactions of the Copper Salts.—M. Denigès.—This reaction depends on the easy conversion of the copper salts into cupric bromide under the influence of potassium bromide and on the dehydration of this product by sulphuric acid, which, when dissolved in an excess of the bromide, displays a fine violet red colour.

On the Sugars of Certain Fungi.—Em. Bourquelot.—The sugars found in the fungi in question are chiefly mannite and trelahose. They often exist together in the same species, though some species contain exclusively one or other of these substances.

Moniteur Scientifique, Quesneville.
March, 1889.

Commercial Museum of Turin.—An account of a useful institution, which, however, contains nothing of chemical interest.

Street-pavements in General, and Cement-Pavements in Particular: with Observations made at Grenoble.—G. Arnaudon.—This memoir also has no decided chemical interest.

Ammonia-soda and the Solvay Process.—A summary of the comparative position and prospects of the Leblanc and the Solvay systems.

A new Process for the Manufacture of Soda.—W. W. Stavely.—From the *Journal of the Society of Chemical Industry*.

Industrial Society of Mulhouse; Session of December 12th, 1888.—Camille Scheen sent in a memoir on the fixation of colours by means of tungstic acid.

Solubility of Barium Sulphite in Hydrochloric Acid.—G. Stillingfleet Johnson.—From the Chemical News.

Decomposition of Nitric Oxide in Contact with Water and Alkaline Solutions—S. Cooke, F.C.S.—From the *Journal of the Chemical Society*.

New Reagent for Iron.—Mr. Venables.—From the Chemical News.

Note on the New Reagent for Iron.—B. Blunt.—From the Chemical News.

On Silicon Hydride.—From the Chemical News.

Crystalline Iron and Nickel Subsulphide.—J. B. Macintosh.—From the Chemical News.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 5. March 5th 1889.

On the Use of Oxygenated Water for Determining Metals of the Iron Group: 1 Chrome.—A. Carnot—Already noticed.

On the Use of Oxygenated Water for Determining Metals of the Iron Group: Chrome, Manganese, and Iron.—A. Carnot.—Already noticed.

A New Method of Determining Lithia by Means of the Fluorides.—A. Carnot.—This memoir will appear in full.

Determinations of Lithia in Mineral Waters: Analysis of two Springs of the Côte d' Or.—A. Carnot.—The springs in question, those of Maizières and Santenay, contain respectively, per litre, 0·0240 and 0·0310 grm. of lithia.

On Diastasic Saccharification.—A. Reychler.—Soluble vegetable albumen acts as a diastase, and its action is intensified by a slight acidity of the solvent.

Transformation of Oleic Acid into Stearic Acid.—P. de Wilde and A. Reychler.—On heating for some hours to 270°—280° oleic acid with 1 per cent of iodine there is formed a mixture of fatty products which after cooling congeal into a solid mass, melting at 50°—55°. From this mixture the authors obtain washings containing about one-third of the iodine used and a watery distillate very poor in hydriodic acid, a distillate of tar, insoluble in alcohol, liquid fatty products, generally very blue, not solidifiable by iodine, and saturating on acidimetric titration only 50 to 60 per cent of the quantity of normal soda calculated for pure oleic acid. A maximum yield of 70 per cent of a solid white acid with a high melting-point. After crystallisation from alcohol this product presents the chemical composition, the melting-point, and all the characteristics of stearic acid. In subsequent operations bromine was substituted for iodine as being more easy of recovery.

Conversion of Erucic Acid into Benic Acid.—A. Reychler.—This conversion has been effected by heating the erucic acid for four hours to 270° in sealed tubes along with 1 per cent of iodine.

Syntheses by means of Cyanacetic Ether, Cyanosuccinic, and Cyanotricarballylic Ethers.—A. Haller and L. Barthe.

Syntheses Effected by means of Cyanosuccinic Ether.—L. Barthe.

Certain Derivatives of Ethyl Acetylcyanacetate.—Alf. Held.—The subject of these three memoirs has been already noticed.

On the Potassium Polysulphides.—W. Spring and J. Demarteau.—The polysulphides K_2S_4 and K_2S_5 cannot be regarded as thiosulphites or thiosulphates.

The Oxidisability and the Cleaning of Tin.—Leo Vignon.—Already noticed.

Some Reactions of the Mercury-Ammonium Chlorides.—In the action of water upon Kane's mercury chloramidide there ensue two inverse reactions, that of the water which tends to produce oxydimercurammonium chloride, and that of ammonium chloride which tends to re-constitute the chloramidide.

Zeitschrift fur Analytische Chemie.
Vol. xxvii., Part 6.

Researches on the Goldenburg Method of Determining Tartaric Acid.—H. Heidenhain.—This bulky memoir is a communication from the laboratory of the New York Tartar Company, and does not admit of reproduction.

The Analysis of Substances Containing Alumina, Lime, and Magnesia.—L. Blum.—This memoir has been already inserted.

Apparatus for the Determination of Carbonic Acid in the Air and in Gaseous Mixtures.—Dr. F. Schydlowski.

Volumetric Determination of Carbonic Acid in Carbonates.—E. Jäger and G. Kruss.—Neither of these papers can be usefully reproduced without the accompanying illustrations.

The Application of Pettenkofer's Bile-Acid Reaction to the Demonstration of Free Sulphuric Acid in Aluminium Sulphate, Alum, &c.—E Egger.—This reaction is obtained when an aqueous solution of cholic acid is heated with sugar and strong sulphuric acid, when there appears a cherry-red solution, becoming purple, and afterwards bluish red. The author finds that 1 c.c. of a mille-normal sulphuric acid = 0·00004 grm. SO_3 if heated in the water-bath with a granule of cholic acid and two drops solution of furfurol (1 drop furfurol in 10 c.c. water) leaves a distinct red stain on the sides of the porcelain capsule in which the solution has been heated or evaporated. In applying this test to alum, 50 grms. of the sample in fine powder are put in a flask, moistened with distilled water, let stand for some hours, covered with a mixture of two parts alcohol and three of ether, shaken well, and set aside. After twenty-four hours the liquid is filtered, the filtrate placed in a capsule, and evaporated down to 1 c.c. on a warer-bath, which must be warmed but not boiling. The cholic acid and furfurol are then added and the colouration is then sought for.

Wine Statistics of Germany.—An elaborate paper of great length, but not calculated to interest our readers.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 2 and 3.

Researches from the Chemical Laboratory of Prof. Alex. Saytzeff at Kasan.—These include a memoir on the oxidation of diallyloxalic acid with nitric acid, and one on the action of sulphuric acid upon diallyloxalic acid, both by P. Bulitsch.

On the Acid Character of the Salts of tne Heavy Metals.—Br. Lachowitz.—The author concludes that for salts of one and the same acid, the less heat is liberated during their formation the greater is their capacity for uniting with bases. For the salts of one and the same metal the more heat is evolved during their formation the greater is their capacity for uniting with bases.

The Constitution of the Fatty Diazo- and Azo-bodies, and on the Formation of Diamide and its Derivatives.—Th. Curtius.—This memoir is not susceptible of useful abridgment.

On Benzoylen-urea and Some of its Derivatives.—W. Abt.—The author here describes the preparation and properties of benzoylen-urea and dimethyl-benzoylen-urea, the preparation of the two monomethyl-compounds, the conversion of α-methyl-benzoylen-urea into dimethyl-benzoylenurea, the action of phosphorus pentachloride upon benzoylen-urea and γ-methyl-benzoylen-urea, and the preparation of diinethoxylquinazoline from β·δ-dichlor-quinazoline.

The Chemical Constitution of Cyanethine and Similar Compounds.—E. von Meyer.—In this preliminary notice the author states that the so-called oxybase of cyanethine formed by the substitution of amide can also be produced by the condensation of equal mols. of propionamidine and α-propionyl-propionic ether. Hence this compound is oxymethyl-diethyl-miazine.

Journal de Pharmacie et de Chemie.
Vol. xix., No. 6.

Syntheses and Reactions of Thiophene.—G. Denigès.—If we wish to reprodnce the well-known reactions of thiophene with isatine, phenanthrene, quinone, alloxane, &c., it is necessary to dissolve these reagents in strong sulphuric acid. A good method for recognising the presence of thiophene in any liquid is to take a glass stirring-rod, with a ball at the end, steep it in the sulphuric solution of one of the reagents, and move it about in the vapour of the liquid under examination. Under these conditions the isatine becomes blue, the phenanthene quinone an intense green, shading into blue, and the alloxane blue. Another reagent, which does not seem to have been noticed, is nitrous sulphuric acid. If benzene, free from thiophene, is added to pure, strong sulphuric acid no colour is formed; with commercial benzene, which always contains thiophene, we have a more or less intense yellow colour, which may pass into brown. In either case, if we add to the acid a trace of a nitrite in solution we obtain on stirring a red colour, much deeper in presence of benzene containing thiophene. But what, above all, distinguishes these two reactions is that on adding water very gradually, and stirring after each drop, the liquid of pure benzene does not change colour, but merely becomes paler. With benzene containing thiophene the colour turns to a violet and even to an intense blue. On adding an excess of water it passes to a brownish green, with a brown precipitate.

Reagents for the Mercaptan Function.—G. Denigès.—Already noticed.

The Assimilation of Milk Sugar.—MM. Bourquelot and Thoisier.—Lactose in the animal economy is converted into glucose. Whether this is directly effected in the digestive channel is not proven.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. iii., No. 34.

Report Presented by Z. Roussin on behalf of the Committee of the Chemical Arts, on a Work Entitled "Manufacture of Colours," by M. Guignet.—The colours spoken of in this work are those used in the various kinds of painting, and in the pigment style of tissue-printing. The work treats more especially of white lead, artificial ultramarine, Guignet's green, and on the use of colours in the different kinds of painting.

Vol. iii., No. 35 and 36.

In these issues there is no chemical matter.

Series 4, Vol. iv., No. 37, 1889.

This number is occupied with an account of the prizes awarded by the Society.

Revue Universelle des Mines et de la Metallurgie.
November and December, 1888.

These numbers contain no original chemical matter.

January, 1889.

Experiments on Grisoutite.—E. Braive.—According to these experiments grisoutite—the composition of which is not given—can be safely used for blasting in "fiery" coal mines, where it neither ignites marsh-gas nor suspended coal-dust.

On the New Hydrocarbon Explosives—J. Henrotte.—An account of the Favier powder of bellite, securite, and roburite.

Vol. v., (3rd Series), No. 2.

This issue contains no chemical matter.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxlii., Part iii.

This number contains no chemical matter.

MISCELLANEOUS.

Detection of Tartaric Acid in Citric Acid.—M. Salzer.—If a solution of citric acid is coloured yellow with a drop of solution of yellow potassium chromate the colour remains unchanged for some days at common temperatures, even if a few drops of sulphuric acid are added. Under the same conditions a solution of tartaric acid converts the yellow chromate into a violet salt of chromic oxide. In cours of a few hours ½ per cent of tartaric acid may thus be recognised in citric acid.—*Revue des Falsifications.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Estimation of Glycerin.—(Reply to "Glycerol").—As nobody else appears to have answered your correspondent's question I beg to refer him for information on quantitative examination of crude glycerin, and detection of impurities objectionable for the manufacture of dynamite, to Sulman and Berry's article in *Analyst*, vol. xi. (1886); Allen's "Commercial Organic Analysis," 2nd Edition, vol. ii.; and Otto Hehner's article in *Journ. Soc. Chem. Ind.*, Jan., 1889 (Quantitative Examination only).—Edward E. Berry.

MEETINGS FOR THE WEEK

Monday, 8th.—Medical, 8.30.
—— Society of Arts, 8. Cantor Lectures. "Instruments for the Measurement of Radiant Heat," by C. V. Boys, F.R.S.
Tuesday, 9th.—Institute of Civil Engineers, 8.
—— Royal Institution, 3. "Before and After Darwin—II. Evolution," by Prof. G. J. Romanes, F.R.S.
—— Sanitary Institute, 8. "Nature of Nuisances, including Nuisances the Abatement of which is Difficult," by J. F. J. Sykes, B.Sc.
—— Society of Arts, 8. "Architecture in Relation to Landscape," by H. H. Statham.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 10th.—Society of Arts, 8. "The Sanitary Functions of the County Council," by Sir Douglas Galton.
—— Pharmaceutical, 8.
—— Microscopical, 8.
Thursday, 11th.—Royal, 4.30.
—— Royal Institution, 3. "Houses and their Decoration from the Classical to the Mediæval Period," by Prof. J. Henry Middleton, M.A.
—— Royal Society Club, 6 30.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
Friday, 12th.—Royal Institution, 9. "On Iridescent Crystals," by Lord Rayleigh, F.R.S.
—— Sanitary Institute, 8. "Sanitary Law—General Enactments, Public Health Act 1875, Model Bye-laws," by A. Wynter Blyth, M.R.C.S.
—— Astronomical, 8.
—— Quekett Club, 8.
Saturday, 13th.—Royal Institution, 3. "Experimental Optics (Polarisation; Wave Theory)," by Lord Rayleigh, F.R.S.
—— Physical, 3. "A Lecture Experiment illustrating the Effect of Heat on the Magnetic Susceptibility of Nickel," and "An Experiment Showing an Effect of Light on Magnetism," by Shelford Bidwell, F.R.S. "On the Dark Flash seen in Some Lightning Photographs," by G. M. Whipple. "On Quartz as an Insulator," by C. V. Boys, F.R.S. "On a Refraction Goniometer," by A. P. Trotter. "Apparatus to Illustrate Crystal Forms," by Prof. R. J. Anderson, M.D.

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THE CHEMICAL NEWS.

VOL. LIX. No. 1533.

ON THE

BEST METHOD OF PREPARING NITROGEN FOR LECTURE PURPOSES.

By CHARLES R. C. TICHBORNE, LL.D., F.I.C., &c.

An article called "A Select Method of Preparing Nitrogen Gas" appeared in the CHEMICAL NEWS, vol. lix., p. 135, and suggested to me the writing of the following communication.

The best method of preparing nitrogen for lecture experiments, or when required in a pure form, is unquestionably (in my opinion) based upon the decomposition of ammonium nitrite. That process possesses numerous advantages over all the others. It is sufficient to enumerate the simplicity of the reaction, the purity of the product, and the ease with which the experiment is performed. The apparatus required is a retort of the right size and a bent tube.

For the last ten years I have been in the habit at my lectures of falling back upon this method when I came to the subject of the oxygen compounds of nitrogen. The symmetric manner in which this reaction harmonises with the production of laughing gas is most instructive, and is a special inducement to use it as a lecture illustration. Here we have the production of a molecule of nitrogen by the splitting up of the nitrite, whilst the nitrate gives us a molecule of the monoxide.

$$NH_4NO_2 - 2H_2O = N_2.$$
$$NH_4NO_3 - 2H_2O = N_2O.$$

A statement in the article (CHEMICAL NEWS, vol. lix., p. 135) runs as follows:—"The action of potassium nitrite, when heated in a suitable apparatus in admixture with ammonium chloride, produces, when prepared cautiously, a moderately pure gas, but, owing to the inconsistence of the reaction, the same is rendered considerably tedious and unprofitable.

As this is contrary to my experience, I think it desirable to give the *modus operandi* which I have adopted, presuming that if the modifications and precautions which I indicate be strictly carried out the experiment will turn out satisfactorily.

Ten grms. of ammonium sulphate and ten grms. of sodium nitrite are mixed in a capacious retort with 40 c.c. of glycerin and 60 c.c. of water. The retort should be of the capacity of half a litre, or about 16 ounces. The retort is placed with the neck elevated to an angle of about forty degrees, so that the water may condense and fall back into the retort. A bent tube is fitted with a cork into the neck, and conducts the gas into a wash-bottle; or it may be collected at once for general purposes without washing.

100 c.c. of water may be used in place of the mixture of glycerin and water, but it does not seem to work quite so regularly. Heat is applied directly to the retort, and the disengagement of free nitrogen begins at a temperature a few degrees below the boiling-point of water. It steadily but rapidly proceeds—the temperature generally rises a few degrees above the boiling-point, but after a little time again begins to fall. A gentle but constant heat will, however, keep up the disengagement of gas until the nitrite is all decomposed. It is desirable to slightly increase the heat towards the end of the reaction.

There is nothing specially new in this process, except the substitution of the sulphate for the chloride, and in the determining of the exact conditions under which the experiment may be carried on successfully for class illustrations, or for the purposes of procuring pure nitrogen with the least expenditure of trouble. If the reaction is pushed on very rapidly ammonia will be evolved, and this phenomenon is most marked when using the chloride in place of the sulphate. If carried on slowly with the sulphate no ammonia is evolved, but a trace of nitrogen dioxide is produced, which may be easily removed by washing with a dilute solution of permanganate of potassium. By carefully regulating the temperature almost pure and neutral nitrogen will be evolved.

A NEW METHOD OF DETERMINING LITHIA BY MEANS OF FLUORIDES.

By A. CARNOT.

THE presence of lithia has been recognised in a considerable number of mineral waters, especially in those rich in alkaline chlorides and carbonates. The methods used to effect its determination leave much to be desired, some on account of their inaccuracy and others on account of the complication and length of the analytical operations. The spectroscope furnishes most valuable indications for the qualitative detection of lithia on account of the extreme sensitiveness of the reaction; but a comparison of the intensity of the spectral rays gives only a doubtful approximation as to the proportion of the metal, especially when it exceeds a few milligrms. per litre.

The reagent which the author employs is ammonium fluoride. It is found in commerce, but it requires to be purified, as it contains silico-fluoride in considerable quantity. For this purpose a few grms. of the salt are dissolved in a small volume of water, a double volume of ammonia is added, the mixture is heated to a boil for a few seconds, let cool, filtered, and washed with ammonia. The silica is thus eliminated, and we have the fluoride in a strong ammoniacal solution. It is kept either in a covered platinum crucible or in a stoppered glass, where it may be left some days without undergoing any change. If there are in solution at most some decigrms. of a lithium salt, with quantities of other alkaline salts not more than ten or fifteen times greater, the author proceeds as follows:—The solution is reduced to a few c.c. in a tared platinum capsule, ammonium fluoride is added, and an excess of ammonia up to 15 to 20 c.c., according to the quantity of the salts. It is well mixed and let settle. There is formed a white gelatinous precipitate of lithium fluoride, scarcely visible and adhering in part to the bottom of the capsule. This is complete by the next morning. Almost all the liquid is decanted through a very small filter and replaced by a few c.c. of ammonia-water with ammonium fluoride. It is stirred up with a platinum spatula and let settle. Soon after a second and a third decantation are made in the same manner and the filter is washed with a few drops of the same reagent. All the soluble alkaline salts are thus removed, and we have, in part on the filter and in part in the capsule, all the lithium salt contaminated merely with ammonia and ammonium fluoride.

The volatile matters are expelled by heating very gently, the filter is burnt, its ash is treated with a few drops of dilute sulphuric acid, and all the liquid is collected in the tared capsule. It is evaporated and gently heated until acid vapours cease to appear, and the neutral lithium sulphate is weighed.

To take account of the solubility of lithium fluoride in the ammoniacal liquid we measure the total volume of the filtrate, which generally ranges from 30 to 50 c.c. We may admit, in accordance with experiments, that 7 c.c. of the liquid contain approximately 2 milligrms. lithium fluoride, corresponding to 4 milligrms. lithium sulphate or 1 milligrm. lithia. The quantity thus calculated is added to that found on weighing.—*Bulletin de la Soc. Chimique de Paris.*

NOTES ON OCHRES, SIENNAS, AND UMBERS.

By GEORGE H. HURST, F.C.S.
Lecturer on Painters' Oils and Colours at the Manchester Technical School.

THE literature on these natural and very valuable pigments is very defective, and consists mostly of vague statements concerning their composition and origin, all evidently copied from one original source which I have not been able to trace. The published analyses of ochres are also vague, and are all more or less variations of one original analysis, and generally take the following form:—Clay 69·5, peroxide of iron 23·5, water 7; and they have led to the erroneous idea that ochres are clays coloured with oxide of iron. Very little attention seems to have been paid by chemists to ochreous colours in general.

Recently I have made several analyses of various ochres, siennas, &c., both as extracted from the earth and as prepared for the market, and it seems to me that these analyses are of sufficient interest to warrant their publication.

Ochres are yellow-coloured earthy pigments, varying in shade from a pale yellow of a brownish hue to a reddish yellow. Siennas are all of a more or less brownish yellow tone. Umbers are of a deep warm brown, ranging from yellowish to reddish shades. They are found naturally associated with gangue, from which they are separated and prepared for use as pigments by a process of grinding, levigating, and drying.

The following fourteen analyses will give some idea of the variety in their composition, due to the differ kinds of rocks in which they are found:—

1. *Oxford Ochre.* Crude, from Shotover Mine.

Hygroscopic water	6·887 per cent
Combined water	8·150 ,,
Lime, CaO	0·998 ,,
Sulphuric acid, SO_3	1·321 ,,
Alumina, Al_2O_3	6·475 ,,
Oxide of iron, Fe_2O_3	12·812 ,,
Silica, SiO_2	63·478 ,,
	100·121

2. *Welsh Ochre.* Crude, unlevigated.

Hygroscopic moisture	2·000 per cent
Water of combination	12·500 ,,
Sulphur trioxide, SO_3	1·315 ,,
Silica, SiO_2	29·725 ,,
Alumina, Al_2O_3	33·315 ,,
Oxide of iron, Fe_2O_3	20·705 ,,
Copper sulphide, CuS	0·515 ,,
	100·075

Of the sulphur trioxide, 0·555 exists as sulphates soluble in water, and of the iron, 0·7655 per cent is soluble in water in the form of ferrous sulphate.

3. *Irish Ochre.* Crude, unlevigated.

Hygroscopic moisture	9·050 per cent
Water of combination	12·000 ,,
*Insoluble SiO_2 and gangue	32·502 ,,
Sulphur trioxide, SO_3	2·685 ,,
Alumina, Al_2O_3	16·770 ,,
Oxide of iron, Fe_2O_3	26·381 ,,
Lime, CaO	0·258 ,,
Copper oxide, CuO	0·630 ,,
	100·260

* This is almost entirely gangue, and can be separated from the ochre proper by levigation.

Of the sulphur trioxide 0·33, of the oxide of iron 0·191, of the lime 0·118, and of the copper oxide 0·228 are soluble in water as sulphates. These are the first recorded analyses of ochres where copper is given as a constituent; to my mind this has a bearing on the question of the origin of these ochres, as I will point out further on.

4. *Derbyshire Ochre.* Levigated.

Water of combination	6·100 per cent
Barium sulphate, $BaSO_4$	20·946 ,,
Silica, SiO_2	4·530 ,,
Calcium sulphate, $CaSO_4$	2·516 ,,
Calcium carbonate, $CaCO_3$	2·755 ,,
Alumina, Al_2O_3	10·655 ,,
Oxide of iron, Fe_2O_3	33·498 ,,
Magnesia, MgO	trace
	100·000

5. *Derbyshire Ochre.* Crude.

Hygroscopic moisture	5·400 per cent
Water of combination	6·000 ,,
Alumina, Al_2O_3	1·040 ,,
Oxide of iron, Fe_2O_3	76·081 ,,
Lime, CaO	0·561 ,,
Sulphur trioxide, SO_3	1·744 ,,
Pyrites, FeS_2	4·783 ,,
Silica, SiO_2 / Barium sulphate, $BaSO_4$	4·394 ,,
	100·000

This is a very red ochre, as might be surmised from the large proportion of iron oxide in it.

6. *Sienna.* Italian.

Hygroscopic moisture	8·250 per cent
Combined water	11·000 ,,
Silica, SiO_2	17·406 ,,
Calcium carbonate, $CaCO_3$	1·075 ,,
Manganese, MnO_2	0·627 ,,
Alumina, Al_2O_3	5·177 ,,
Oxide of iron, Fe_2O_3	57·032 ,,
	100·567

This is a very light sienna, almost approaching ochre in tint, much lighter than might have been expected from the amount of iron in it.

7. *Raw Sienna.* Italy.

Hygroscopic water	17·550 per cent
*Water of combination	9 000 ,,
Silica, SiO_2	22·656 ,,
Calcium carbonate, $CaCO_3$	0·960 ,,
Manganese, MnO_2	1·190 ,,
Alumina, Al_2O_3	2·840 ,,
Oxide of iron, Fe_2O_3	45·820 ,,
	100·016

Raw siennas are brownish yellow in colour, and differ from ochres, which are yellow or reddish yellow, in yielding orange-red pigments on calcining, whereas ochres yield deep reds.

8. *Burnt Sienna.* Italy.

Hygroscopic water	9·450 per cent
*Water of combination	3·275 ,,
Silica, SiO_2	36·912 ,,
Manganese, MnO_2	traces
Calcium carbonate, $CaCO_3$	1·233 ,,
Alumina, Al_2O_3	3·480 ,,
Oxide of iron, Fe_2O_3	45·650 ,,
	100·000

* See note, next page.

9. *Raw Sienna.* Probably Italian.

*Water of combination	9·400 per cent
Hygroscopic water	12·400 ,,
Silica, SiO_2..	5·016 ,,
Calcium carbonate, $CaCO_3$ ..	4·460 ,,
Alumina, Al_2O_3..	7·265 ,,
Oxide of iron, Fe_2O_3	59·695 ,,
Manganese, MnO_2	1·465 ,,
Magnesia, MgO..	trace
	99·701

10. *Umber.* From Cyprus.

Hygroscopic moisture	4·325 per cent
Water of combination	8·450 ,,
Silica, SiO_2..	29·564 ,,
Calcium carbonate, $CaCO_3$ ..	5·560 ,,
Manganese, MnO_2	12·285 ,,
Alumina, Al_2O_3	2·735 ,,
Oxide of iron, Fe_2O_3	36·475 ,,
	99·394

11. *Umber.* Derbyshire, Crude.

Hygroscopic water	13·475 per cent
Water of combination	5·175 ,,
Barium sulphate, $BaSO_4$	30·105 ,,
Silica, SiO_2	4·430 ,,
Calcium sulphate, $CaSO_4$.. ..	2·153 ,,
Calcium carbonate, $CaCO_3$ ..	2·607 ,,
Alumina, Al_2O_3	8·078 ,,
Oxide of iron, Fe_2O_3	22·500 ,,
Manganese, MnO_2	11·530 ,,
Phosphoric acid	trace
	100·053

12. *Umber.* Probably English.

Hygroscopic water	6·612 per cent
Water of combination	10·250 ,,
Calcium sulphate, $CaSO_4$.. ..	2·137 ,,
Calcium carbonate, $CaCO_3$ ..	6·090 ,,
Alumina, Al_2O_3	12·802 ,,
Oxide of iron, Fe_2O_3..	29·983 ,,
Manganese, MnO_2	7·110 ,,
Silica, SiO_2	24·518 ,,
	99·502

13. *Ochre.* Cornwall.

Hygroscopic moisture	1·40 per cent
Combined water	10·00 ,,
Silica, SiO_2	59·67 ,,
Alumina, Al_2O_3	9·72 ,,
Oxide of iron, Fe_2O_3	18·54 ,,
Lime, CaO	0·23 ,,
	99·56

14. *Ochre.* French.

Hygroscopic moisture	1·80 per cent
Combined water	9·20 ,,
Silica, SiO_2	54·00 ,,
Alumina, Al_2O_3	13·75 ,,
Oxide of iron, Fe_2O_3	20·73 ,,
Lime, CaO	0·19 ,,
	99·67

These last two analyses are not original, but are quoted from recently published results.

* This includes small quantities of organic matter which are present in siennas, and to which their peculiar brownish yellow colour and their yielding orange-red pigments on calcining is probably due. The amount of this organic matter has not been separately determined. Siennas also contain small quantities of manganese, which also will influence the shade of the pigment.

Terra Verte is a natural green-coloured pigment of which, also, but vague descriptions are to be found in text-books. A sample which was recently sent me had the following composition :—

Hygroscopic moisture	1·450 per cent
Combined water..	3·650 ,,
Oxide of iron, Fe_2O_3	26·870 ,,
Alumina, Al_2O_3	3·165 ,,
Manganese, MnO_2	trace
Lime, CaO	2·065 ,,
Silica, SiO_2	52·120 ,,
Magnesia, MgO	10·665 ,,
	100·000

It was very hard, broke with a conchoidal fracture, of a waxy lustre and soapy feel. Acids had but slight action on it. From its physical properties and chemical composition I consider it to be the mineral bronzite, and is essentially a ferrous magnesium silicate.

It would be of interest to ascertain the origin of ochres, siennas, and umbers. On this point nothing, or but little, is definitely known, and it can only be arrived at by ascertaining the conditions in which deposits of ochres are found, knowledge which we are not yet possessed of. I cannot myself add much on this point, but from my examination of the ochres—the results of which are recorded above—I am of opinion that they must be classed as alteration-products consisting of earthy substances coloured to a more or less extent by hydrated peroxide of iron and manganese, which latter bodies have been produced by the oxidation and hydration of other iron ores or minerals, such oxidation-products having become incorporated by some means with the earthy bodies. That this may be the origin of ochreous deposits is in my opinion indicated by some of the analyses of ochres I have made. The crude Welsh and Irish ochres both contain copper, the former in the form, I think, of sulphide, the latter in the form of sulphide and sulphate. Both contain ferrous sulphate in small quantities, which lead me to think that these ochres have been formed by the oxidation and hydration of cupreous iron pyrites. In the case of the crude Derbyshire ochre No. 5 I have recognised pyrites in this, and I know that this ochre to prepare it for the market, undergoes a process of levigation, during which much pyrites is separated. The combination of the oxide of iron with the other constituents or earthy matter of the ochre is almost always a physical one, and not a chemical combination. By treatment of many crude ochres with acid the oxide of iron can be dissolved, leaving the earthy matter behind very often in the form of small fragments of mineral, which can be recognised as the basic rock of the district wherein the ochre was found. The Irish ochre No. 3 is one of this character.

In the case of the Italian siennas and ochres, I have information that they are found in basins which have evidently been filled at some period with water, and that into these basins have flowed streams of water carrying down a quantity of ferruginous matter derived from deposits of hæmatite iron ore situated above the deposits of ochre. Along with the ferruginous matter there have also been carried down by the same streams the debris of the rocky base and other products of the destructive action of the weather on the rocks and soil immediately above the basin; these were gradually deposited, aud the deposit in time filled up the basin and formed the sienna and ochre which is now quarried. These deposits are not pre-human, for in them have been found arrow-flints, bronze idols, products of the industry of some bygone races of men.

Besides the points of distinction between ochres and siennas above pointed out there seems to be another one. While siennas are invariably, as stated above, found in large masses of a homogeneous structure, all of which

is utilised for pigment purposes, and which have been formed of the debris due to the denudation of rocks and mineral masses not immediately surrounding the deposit of sienna, ochres seem to have been formed *in situ* by the oxidation of iron pyrites and other iron minerals, the products of such oxidation impregnating the surrounding rock masses to form the colouring-matter as we know it, and which has to be separated by lixiviation and levigation to fit it for pigment purposes.

Of umbers I am unable to bring forward anything bearing on their origin, but I am of opinion that in this particular they resemble the siennas rather than the ochres.

I trust that the little I have been able to add to the knowledge of these valuable pigments will induce some one to come forward with other facts of interest about them, and I for one will be only too glad to welcome such contributions.

Chemical Laboratory,
22, Blackfriars Street, Manchester.

THE EFFECTS OF VOLTAIC ELECTRICITY TOWARDS GERMINATION.

By H. N. WARREN, Research Analyst.

The following effects of voltaic agency towards germination were observed:—

During the previous summer, in my laboratory, four constant ferric chloride cells were arranged, with their respective wires terminating in thin platinum plates of about four inches in length by two wide. Over these was spread, about two inches in thickness, cotton soaked in a dilute solution of salt water, and, sprinkled over the surface of the same, common mustard seed (*Sinapis alba*). In less than twenty-four hours germination over the positive plate was distinctly visible. At the end of three days this was much more distinct, and after a week's duration it had assumed an altitude of upwards of one inch in height and of an intense green colour, whilst those confined to the negative plate, and which, up to this period, had only commenced germinating, and which were possessed of an almost pure white colour, and far more backwards as regards growth. At this period the current was now reversed, that which had previously been the positive plate becoming the negative, and *vice-versâ*. After the further lapse of a few days exactly a reverse phenomenon presented itself; those which had apparently flourished so well when influenced by the positive current, now gradually became bleached of their colour, and speedily withered, whilst the opposite seeds, invigorated by the removal of the opposing current, gradually assumed a green tint, and rapidly commenced to flourish, which nevertheless, together with those on the opposite plate, speedily afterwards withered, and refused to be stimulated on renewing a more intense current.

The rapid bleaching of those situated in the neighbourhood of the negative plate may, I think, be accounted for by the small but constant liberation of chlorine gas, thus enveloping them in an atmosphere of the same, or otherwise retarding germination when in a nascent state.

The experiment becoming terminated, the two platinum plates, in connection with their respective electromotors, were next introduced into a tank containing pond water, having been previously examined microscopically. After the current had been maintained for about six hours, on again presenting it before the microscope for further examination, several living organisms were observed, which increased in kind and number as the experiment proceeded. A few grains of salt were now introduced into the water in order to render it still more able to conduct the current. On a powerful secondary charge being now transmitted into it by the aid of a large induction coil, and a re-examination made, no living organisms were observed, and the experiment was allowed to proceed as before, re-producing further quantities of living organisms.

The experiments were here interrupted, and are now under further investigation.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1889.

Mr. WILLIAM CROOKES, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Kitchen, Beech Grove, Ulverston; John Edmund Legg, Elm House, Great Berkhamstead, Herts; Walter J. Sykes, 47, Ouseley Road, Balham, S.W.; William Virtue, The Laboratory, Crosswells Brewery, Oldbury.

26. "*The Molecular Weights of the Metals.*" Preliminary Notice. By WILLIAM RAMSAY, Ph.D., F.R.S.

The molecular weights of a number of metals have been determined by Raoult's vapour-pressure method, viz., by ascertaining the depression of the vapour-pressure of the solvent produced by a known weight of dissolved substance. The connexion between osmotic pressure and depression of vapour-pressure has been shown by van't Hoff, and in a recent number of the *Zeitschrift für Physikalische Chemie*, by Arrhenius; the method of the latter is characterised by great simplicity. It has also been mathematically developed by Planck (see also *Zeitschr. f. Phys. Chem.*, 1888, 405).

The relation between molecular weight and depression is expressed by the equation—

$$W = \frac{W' \times P \times p}{100 \times d},$$

where W is the molecular weight to be found; W' the molecular weight of the solvent; P/100 the percentage weight of the dissolved substance in solution; p the vapour-pressure of the solution; and d the depression in the vapour-pressure of the solvent produced by adding the substance dissolved. It will be noticed that the relation is independent of temperature.

The solvent employed was liquid mercury; the temperature 260° and 270° for a few substances, and the boiling-point of mercury for most. The apparatus, of which a description will appear in the complete paper, is of the simplest description, and lends itself to the

Element.	Atomic weight.	Molecular weight. Found.	Molecular weight. Calulated.	Molecular formula.
Lithium	7·02	7·00	7·02	Li_1.
Sodium	23·04	12·1	11·52	$Na_{\frac{1}{2}}$.
Potassium	39·14	28·57	?	K_1 (?).
Silver	107·93	109·0	107·93	Ag_1.
Gold	197·22	204·3	197·22	Au_1.
Barium	137·0	74·45	68·5	$Ba_{\frac{1}{2}}$.
Magnesium ..	24·3	20·33	24·3	Mg_1.
Zinc	65·34	60·85	65·43	Zn_1.
Cadmium	112·1	100·0	112·1	Cd_1.
Gallium	69·9	68·1	69·9	Ga_1.
Thallium	204·2	183·5	204·2	Tl_1 (?).
Tin	119·1	114·9	119·1	Sn_1.
Lead	206·93	204·1	206·9	Pb_1.
Antimony	120·2	134·2	120·3	Sb_1.
Bismuth	208·1	209·2	208·1	Bi_1.

determination of molecular weights of all substances soluble in any pure menstruum; no knowledge of the vapour-pressures of the solvent being required. The method is much more generally and easily applicable than the alternative method of Raoult, whereby the molecular weight is deduced from the depression of the melting-point of a solvent due to dissolved substance.

The results obtained are given in the Table (see preceding page).

These numbers represent some of the actual results. Nevertheless, they must not be taken as absolute; although in many cases they are conclusive as to the molecular weight of the metal, still further experiments are needed. As an instance of what occurs, the metals thallium and antimony may be chosen. With thallium, for example, the following results were obtained:—

Percentage of thallium in amalgam.	Molecular weight. Found.	Calculated.
0·8191 p. c.	157·4	204·2
1·666 „	183·5	204·2
2·894 „	174·3	204·2
3·290 „	183·9	204·2

No appreciable change is produced on concentration. But with antimony the molecular weight increases proportionately to the amount present, thus—

Percentage of antimony in amalgam.	Molecular weight. Found.	Calculated.
1·117 p. c.	134·2	120·3
1·526 „	155·4	120·3 to 240·6
2·257 „	193·4	120·3 to 240·6
3·289 „	294·6	240·6 to 481·2 ?

Here an association of atoms is evidently in progress.

It may appear startling that the molecular weight of the metals sodium, potassium, and barium are given as half their atomic weights. From the formula employed in calculation it will be seen that this is on the assumption that the molecular formula of mercury is Hg_1. There are strong reasons in favour of this supposition, and the whole question will be discussed in the complete paper. But at present it may be taken as the most convenient way of stating results. The author would not wish to commit himself to any positive assertion on the point, except in so far as the accuracy of the experimental data are concerned. The numbers have been amply confirmed by repetition, and must be taken as accurate within from 1 to 5 per cent of the quantity measured.

The author is now occupied in extending these results, and in confirming them by the depression of the melting-point method.

27. "*The Application of Raoult's Depression of Melting-point Method to Alloys.*" By C. T. Heycock, M.A., and E. H. Neville, M.A.

The result of Raoult's investigations on the lowering of the freezing-points of solutions, "that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever lowers the freezing-point of that solvent 0·62 C.," has not apparently been tested by the dissolution of metals in metals.

The authors therefore present the results of some preliminary experiments on the change in the solidifying point of tin caused by the addition of small quantities of other metals. From repeated experiments they have confidence that the numbers obtained are approximately correct, though they reserve for a future paper details of the method of experiment and the conclusions which may be drawn from the results. For the present, it is sufficient to state that the dissolution of a metal in tin appears to follow the same laws as that of compounds in other solvents, *i.e.*, (1) That the fall in temperature of the solidifying point is directly proportional to the weight of metal added. (2) That the fall of temperature is inversely as the atomic (molecular ?) weight of the metal added. The experiments were conducted by melting a mass of 400 grms. of tin, and by means of a mercury thermometer, using a reading telescope, the solidifying point was determined whilst the mass was kept rapidly stirred. Slight surfusion, usually three or four-tenths of a degree, was generally noticed. The tin was then re-melted, and from one to three grms. of metal added, and the solidifying point again determined. In some cases where the metals alloy with difficulty, portions of the 400 grms. of tin were withdrawn, and, whilst fused under borax in a gas furnace, known weights of the other metals were added, and then this concentrated alloy was added to the bulk of the tin. Another grm. or two of the metal was then added, and the experiments repeated. The average melting-point of the tin used was 226·4° C. Working as above described, the authors find one atomic proportion of each of the following elements dissolved in 100 atomic proportions of tin causes the following falls of temperature:—

Zn	2·53°
Cu	2·47
Ag	2·67
Cd	2·16
Pb	2·22
Hg	2·3
Al	1·34
Sb	2·0 (rise).

The facts that aluminium produces a fall only one-half that of the other elements, and antimony produces a rise, are they think of especial importance.

They hope shortly to communicate a more complete paper to the Society, and intend using other solvents such as Na, Cd, Pb, Hg, &c. They also propose to investigate the behaviour of those alloys which appear to be true compounds, and to find out to what extent of concentration the fall of temperature remains proportional to the weight of metal added, &c.

Discussion.

Dr. Armstrong said that notwithstanding the apparent regularity and simplicity of the results, he was not prepared to accept them as in the least degree final. There was not sufficient evidence in his opinion that the effect observed was not in part at least the outcome of a change in the molecular composition of the solvent; this objection had already been formulated by himself as well as by Professor J. J. Thomson, and no one had as yet replied to their criticisms (*cf. Brit. Ass. Report*, 1888; *Report of Electrolysis Committee*). The question was one of fundamental importance in relation not only to the determination of molecular weights of dissolved substances, but also to the interpretation of the phenomena of electrolysis and chemical change generally. The results obtained by Raoult's methods were, he thought, comparable with those obtained by determining the specific heats of elements; in the latter case the observations were undoubtedly made with masses of molecules, which probably were of varying degrees of atomic complexity (*cf. Brit. Ass. Report*, 1885, p. 962), and yet the results were found to be such as to justify conclusions being drawn as to the relative magnitudes of their fundamental constituents—the atoms. In the same way it was possible that the results obtained by Raoult's method by means of observations on the behaviour of molecular complexes might afford the means of deducing the relative magnitudes of the fundamental molecules comprising the complexes, but not of the actual complexes operated with. The formation of compounds which undoubtedly took place in the case of sodium, for example, must influence the results.

Mr. Crompton asked Professor Ramsay whether he had examined solutions of strengths other than those given. He drew attention to Beckmann's recent experiments on the lowering of the freezing-point; these show that the true molecular weight was only obtained when

solutions were used the concentration of which was allowed to vary only within certain narrow limits; and that if the solutions were too dilute the molecular weight obtained from the lowering of the freezing-point was too low, while, if the solutions were too concentrated, it was too high. In some cases the variation of the number obtained with the concentration was enormous. The same would probably be the case for the reduction of the vapour-pressure. The results brought forward were undoubtedly of the greatest interest, but he thought that the method had not been so thoroughly investigated as to give them an absolute value as molecular weight determinations.

Mr. PICKERING said that when the freezing-points of mixtures of sulphuric acid and water were plotted out in a form which should, according to Raoult, give a straight line, they gave a most irregular figure. Between 0 and 100 per cent the solidifying point sunk twice below −40°, and rose twice to +10°. The extreme end of the figure (for weak solutions) is, no doubt, irregular and curvilinear like the rest of it, and can be called straight only because the irregularity and curvature are lost in the comparative magnitude of the experimental error. It was not fair to consider evidence deduced from such a source in the same light as that deduced from gaseous densities, where any appreciable deviation from straightness is found only at the extreme ends of the figure, and where the deviation is of the same regular character in every case.

Mr. GROVES suggested that although compounds of the metals and mercury could be formed, it was possible that these underwent dissociation when dissolved in mercury.

Professor CAREY FOSTER remarked, that in the case of weak solutions the temperature at which ice forms is determined; but in the case of stronger solutions the temperature is often that at which a hydrate forms: this probably was the explanation of the peculiar curve described by Mr. Pickering. Much depended on the definition given of a molecule, whether it is defined as that smallest quantity capable of existence *per se*, or as that quantity which produces a given effect in depressing vapour-pressure, or freezing-point, &c. The two magnitudes were not necessarily the same. The relation observed could hardly be accidental; yet he thought that the value obtained might be a quantity connected with the molecular weight, but not necessarily identical therewith.

Mr. HOWARD said the main question was, did compounds of mercury with the metals exist at the high temperatures at which the observations were made.

Professor RAMSAY, in replying, argued that the existence of a compound of the metal with the solvent—in this case mercury—would give an increased molecular weight; and that, although such compounds existed in many cases at low temperatures, yet, at the boiling-point of mercury, they appeared to be decomposed. The compound of copper and mercury, however, was an exception, inasmuch as it was not dissolved to any great extent by boiling mercury. Hence experiments with copper could not be carried out.

Substances in dilute solutions must be regarded as in the gaseous state, their molecules being so far distant from each other as not to exert appreciable attraction on each other; and as occupying but a small portion of the space they inhabit. It has long been argued that the molecular complexity of the gases, hydrogen, oxygen, and nitrogen, must be the same, inasmuch as these elements have equal coefficients of expansion within the widest limits of temperature. A similar argument applies to substances in dilute solutions; it is much more probable that they have a simple and similar molecular structure than that the molecules, if complex, dissociate to an equal extent on equal rise of temperature or on equal alteration of concentration.

As regards the empirical nature of Raoult's laws, it is paralleled by the empirical nature of Boyle's and Gay-Lussac's laws, that is, such laws are merely approximations to truth, and depend on the fact that the molecules are sensibly beyond the sphere of each other's attraction, and themselves occupy no appreciable space. Hence their inapplicability at high concentrations. Just as gases deviate at high pressures from the laws of elasticity when definite compounds are formed, as instanced by Mr. Pickering in the case of mixtures of sulphuric acid and water, each compound acts as a homogeneous substance—as a solvent of definite molecular weight, with a definite melting-point, which is lowered by the addition of one or other constituent, though probably not to a similar extent, owing to further reactions between the solvent and the added constituent, water or sulphuric acid, as the case might be.

28. "*Some Compounds of Tribenzylphosphine Oxide.*" By N. COLLIE, Ph.D., F.R.S.E.

Some time ago the author, in conjunction with Prof. Letts, published an account (*Trans. Roy. Soc. Edin.*, xxx., Part I., 181) of the salts of tetrabenzylphosphonium. One of the compounds mentioned, the oxide of tribenzylphosphine, has been further examined. When treated with fuming nitric acid, tribenzylphosphine oxide yields a trinitro-derivative $(C_7H_6{\cdot}NO_2)_3PO$, which is probably reduced by the action of tin and hydrogen chloride to a triamido-derivative. If the oxide be heated at 170° C. with sulphuric acid, a trisulphonic acid results,—

$$(C_7H_6{\cdot}SO_3H)_3PO.$$

In both cases the introduced group takes up the para-position, as on oxidation *p*-nitrobenzoic and *p*-sulphobenzoic acids are obtained. On treatment with acetyl chloride the oxide yields a simple addition product, $(C_7H_7)_3PO{\cdot}C_2H_3OCl$. It also combines with hydrogen chloride and bromide, yielding compounds of a complicated structure agreeing with the corresponding triethylphosphine oxide-derivative, *e.g.*, $5(C_7H_7)_3PO{\cdot}4HCl$.

Tribenzylphosphine oxide therefore differs in several respects from the oxides of the tertiary phosphines of the fatty series. It does not form such stable compounds, neither is the oxide itself capable of resisting oxidising agents to the same extent. On the other hand, however, some of the derivatives, although complicated in their structure, seem to be analogous to the corresponding derivatives in the fatty series.

DISCUSSION.

Professor RAMSAY drew attention to the remarkable composition and stability of the malecular compounds obtained by Dr. Collie; he thought it was becoming essential to include and discuss such molecular compounds in a special chapter.

29. "*Contributions to Our Knowledge of the Isothiocyanites.*" By AUGUSTUS E. DIXON, M.D.

The author describes a number of compounds obtained from various thiocarbimides by combination with basic substances.

The first two are members of the little known series of benzylated thiocarbamides. *Ethylbenzyl thiocarbamide*, EtNH·CS·NHBz, from ethyl thiocarbamide and benzylamine, crystallises in white needles melting at 102—103°. The corresponding *phenylbenzyl thiocarbamide*,—

PhNH·CS·NHBz,

forms short thick prisms; m. p. 153—154°.

The next three compounds are semithiocarbazides, and are obtained by the action of phenylhydrazine on the corresponding thiocarbimides. *Ethylphenyl semithiocarbazide*, EtNH·CS·NH·NHPh, forms glassy prisms melting at 121—122° without decomposition. A very delicate test for this substance consists in adding a few drops of ferric chloride to its solution in alcohol; a blood-red colour is produced, changing rapidly to dark green. It is remarkable that the m. p. of a metameric compound, PhNH·CS·NH·NHEt, obtained by Fischer (*Annalen*, cxcix., 296) is much lower, viz., 109—110°. *Acetylphenylsemithiocarbazide*, AcNH·CS·NH·NHPh, forms thick

white prisms melting at 178—179°, while the analogous *benzoylphenylsemithiocarbazide*,—

$$PhCO\cdot NH\cdot CS\cdot NH\cdot NHPh,$$

crystallises in silky asbestos-like needles, which do not melt at 220°.

The remaining compounds (together with the two last mentioned) were obtained during an investigation of thiocarbamides containing *acid* radicles, viz., *acetylorthotolylthiocarbamide*, AcNH CS·NHTo, which crystallises in lemon-yellow prisms, m. p. 184°; and *benzoylphenylethylthiocarbamide*, PhCO·NH·CS·NEtPh, which crystallises in yellow prisms melting at 133—134°.

30. "*The Constitution of Primuline and Allied Sulphur-compounds.*" By Arthur G. Green.

The product obtained on heating two mol. props. of paratoluidine with two atomic props. of sulphur until the evolution of hydric sulphide has ceased, chiefly consists of a mixture of Merz and Weith's thiotoluidine (diamidoditolyl sulphide, $(C_7H_6\cdot NH_2)_2S$), and a base, $C_{14}H_{12}N_2S$, containing four atoms of hydrogen less, which, as proposed by Jacobsen, may be called "dehydrothiotoluidine." If the amount of sulphur be doubled, thiotoluidine is almost absent, the product containing, together with dehydrothiotoluidine, a more highly condensed base, which probably has the formula $C_{28}H_{18}N_4S_3$. The monosulphonic acid of the latter base possesses the peculiar property of readily dyeing unmordanted cotton in an alkaline bath a pure primrose-yellow, and whilst on the fibre may be converted into a diazo-compound which may there and then be caused to interact with amine and phenols. This product, discovered by the author in February, 1887, was put on the market under the name of "Primuline," and is largely employed by cotton-dyeing on account of the great range of fast shades that may be obtained with it.

Dehydrothiotoluidine, $C_{14}H_{12}N_2S$, is isolated from the melt by boiling with somewhat diluted chlorhydic acid, precipitating with soda, distilling, and crystallising from amyl alcohol. It forms long, yellowish, iridescent needles melting at 191° (uncorr.), and boils at 434° (uncorr., bar. 766 m.m.). It is moderately soluble in hot amyl alcohol, readily in acetic acid. Its alcoholic solution exhibits a violet-blue fluorescence, which also characterises all its derivatives. By diazotisation, and by the constitution of the acetyl-derivative, it is shown that one of the nitrogen atoms is in the form of NH_2, whilst the other is nitrilic. By boiling with zinc-dust and HCl it is reduced to a base of quite different properties. On distillation with zinc-dust it yields paratoluidine. From these and other facts the author deduces the formula—

$$CH_3\cdot C_6H_3\langle{}^{N:CH}_{S}\rangle C_6H_3\cdot NH_2,$$

which represents dehydrothiotoluidine as derived from thiotoluidine by removal from a CH_3 and an NH_2-group of four atoms of hydrogen.

The *acetyl-derivative*, $C_{14}H_{10}SN(NH\cdot CO\cdot CH_3)$, forms white prisms which melt at 227° (uncorr.). It combines with bromine. The *dimethyl-derivative*,—

$$C_{14}H_{10}SN\cdot N(CH_3)_2,$$

crystallises in yellowish plates melting at 195—196°. The *trimethylammonium* salts are easily soluble in water and have strong tinctorial power, dyeing silk a pure greenish yellow with a green fluorescence. The *monosulphonic acid*, $C_{14}H_9SN(NH_2)(SO_3H)$, crystallises from water either in flattened, yellow needles $(+H_2O)$, or in orange, aggregated leaflets $(+2H_2O)$. The salts of the sulphonic acid are mostly colourless, and have no affinity for cotton. The ammonium and copper salts are very characteristic: the latter is an insoluble reddish brown precipitate; the former crystallises in sparingly soluble, white, crystalline plates.

Primuline-base.—As this compound is also obtained by heating thiotoluidine or dehydrothiotoluidine with sulphur, it would appear that its formation is preceded by that of these compounds. The difficulty of isolating it in the pure state has hitherto prevented the determination of its composition with certainty, but it appears to have the formula $C_{28}H_{18}N_4S$, and hence probably has the constitution—

$$CH_2\cdot C_6H_3\langle{}^{N:CH}_{S}\rangle C_6H_2\langle{}^{N:CH}_{S}\rangle C_6H_2\langle{}^{N:CH}_{S}\rangle C_6H_3\cdot NH_2.$$

Primuline-base is a bright yellow powder, which is nearly insoluble in all solvents. Its salts are dark-coloured and are decomposed by water, in which they are insoluble. It is an extremely stable compound, and may be heated above 400° C. without decomposing.

Discussion.

Mr. Wynne took exception to the formulæ proposed by Mr. Green, regarding it as improbable that dehydrothiotoluidine contained a closed chain of eight atoms, and that the sulphur-atom should be connected in the ortho-position in the one and the meta-position in the other nucleus.

(To be continued).

NOTICES OF BOOKS.

Cosmic Evolution; being Speculations on the Origin of our Environment. By E. A. Ridsdale, Associate of the Royal School of Mines. London: H. K. Lewis.

We have here a thoughtful and weighty little book, *multum in parvo*, in a very different sense of the words from that applied to waistcoat pocket manuals. The author disclaims the introduction of any novel facts, but hopes, and that with good reason, that he has shown among well-known facts a relation which has been hitherto overlooked. His object is one with which we most thoroughly sympathise. He seeks to prove that Evolution is not merely the law of the heavens, as it has been shown by Kant, La Place, and Herschel; not only of the process by which organic species are formed, according to Lamarck and Darwin, but of the material from which stars and organisms are ultimately composed: of matter itself. The attempt may seem bold, but we are convinced that it will ultimately prove successful. He introduces a capital conception, the "survival of the most inert," which plays in the origin and history of chemical compounds a part very similar to that played by the "survival of the fittest" in the life-history of organisms. We know that among animals and plants such forms as are most in harmony with their surroundings survive, whilst those less perfectly adapted are either modified or disappear. In a very similar manner bodies which, taken as wholes, are most inert, and which consequently are least likely to be decomposed by the action of surrounding bodies, will remain. On the contrary, those bodies which are the least inert will gradually tend to disappear, and, unless continually re-created, must in time vanish from the globe. This part of his subject, its chemical aspect, Mr. Ridsdale works out very ably. That such a survival of the most inert is actually taking place he shows by reference to phenomena commonly witnessed:—"In Nature's vast laboratory, as in our small experimental ones, there is a constant tendency for barium salts to form sulphates; magnesium and aluminium salts, oxides and silicates silver salts, chlorides; lead salts, sulphides; &c. The stable or inert salt, when formed, remains—except under exceptional circumstances; but any other salt . . . . is broken up, sooner or later, by contact with some unfavourable environment." We have, he considers, a strong presumption that many, if not all, the so-called "elements" are elemental only inasmuch as we have not yet been able to place them among a sufficiently powerful set of conditions. He considers that the bodies formed earliest must have been the simplest, and that those

originating later must have been of a more complex constitution and of greater atomic weight. His views are in harmony with certain well-known facts. Thus, in the groups of the elements the most active are usually those with the lowest atomic weights; that there are greater gaps in the amounts of the later-formed elements than in those of the earlier-formed ones; that the elements with the lower atomic weights are more plentiful and more generally distributed than those with higher weights.

The second chapter takes up the organic aspect of Evolution. Concerning life he remarks:—"How it arose we know not; whether it was latent from the beginning, and, oppressed hitherto by the dominant environments, only awaited a period of quiescence to come into operation, or whether it was induced by a special act of Creation we cannot tell." He holds that the earlier forms of life showed a great similarity to the inorganic, from which it has only been differentiated by slow degrees. He considers that in the organic, as in the chemical sphere, the tendency to variation is now dying out. The fact that we can in no way now produce life from inorganic forms, *because we cannot reproduce* the conditions, just as we cannot transmute lead into gold, is a proof of the correctness of the theory of Evolution.

In the third chapter we have the general aspect of Evolution. He rejects the teachings of those physicists who deny to the sun a birthday more than twenty million years distant, as inadequate to account for the facts of terrestrial geology. In this rejection he will be joined by the majority of biologists as well as geologists, who may at any rate claim the right to wait until mathematico-physicists have learned to bring their discordant conclusions into harmony and to demonstrate their fundamental assumptions.

We cannot further prolong our examination of this interesting little work, but we must strongly recommend it to our readers.

Practical Organic Chemistry; the Detection and Properties of Some of the More Important Organic Compounds. By S. Rideal, D.Sc., F.C.S., F.I.C., F.G.S. London: H. K. Lewis.

This little manual is avowedly written with especial reference to the wants of medical students, and accordingly those compounds are brought into prominence with which he is likely to come most in contact. Under each it is stated whether it occurs in the preparations of the British Pharmacopœia or not, and, in the former case, into what preparations it enters. The most characteristic reactions are marked with an asterisk, and to a few, said to be new to English text-books, the name of the discoverer is added in brackets. Some of these are likely to prove useful. We find no mention of certain artificial alkaloids which—whether permanently or as a transient freak of fashion—are finding their way into medical practice.

The aim of the book, as it will be seen at once from the preface, is distinctly examinational. "The student," we are told, "*reading* for the London University Examinations—B.Sc. and Inst.M.B.—will find all the substances mentioned in the Syllabus of the University discussed at length." We beg to call passing attention to the word we have italicised. Like not a few other persons in these days, we should like to see the highest University honours gained not by *reading* but by *working*—in other words, by the power of origination. We here venture to refer to an instance of the examinational spirit. Two youths, at one of our great public schools, had sent in essays on a certain occasion. The judges did not award the prize to the author of the essay they thought the best, but to his rival, because the latter had quoted thirteen books instead of thinking the matter out independently! We do not think that even the Chinese official examiners could improve upon such a procedure.

The Lixiviation of Silver Ores with Hyposulphite Solutions, with Special Reference to the Russell Process. By C. A. Stettefeldt. New York: Scientific Publishing Co.

The author of this book seeks to expound the so-called lixiviation process for silver ores, as compared with amalgamation. He describes the old method of lixiviation with sodium hyposulphite, as introduced by Von Patera and developed by Kiss and Kuestel, but admits that it was not free from grave defects. Of these, perhaps the most important is its inability to deal with silver glance and the antimonial and arsenical silver sulphides. Hence he recommends the adoption of the lixiviation process as modified by E. H. Russell. This metallurgist employed a double sodium-copper (cuprous) hyposulphite, and thus overcame many of the difficulties which beset Von Patera's original method. Mr. Stettefeldt then gives an elaborate comparison of the two lixiviation processes and of Russell's improved lixiviation as against amalgamation. He contends that the percentage of silver extracted is in most cases higher than that gained by amalgamation; that the chemicals used in the process cost less than the value of the wasted mercury and the wear and tear of the pans; that lixiviation allows of the extraction of copper and lead, and in many cases of more gold than is secured by amalgamation, which latter process is, further, injurious to the health of the workmen. The chief defects of lixiviation here recognised are that the precious metals are obtained as sulphides, which require a more difficult and costly treatment than does amalgam.

The author considers that all silver ores which do not contain a large percentage of lead or copper can be successfully dealt with by lixiviation.

In describing the chemicals used in the lixiviation process Mr. Stettefeldt explains the different manners in which the strength of alkali is expressed in England, France, and Germany. The persistent use in English technical circles of 24 as the atomic weight of sodium in place of 23—a custom utterly indefensible, but against which chemists are powerless—he characterises as "one of the numerous mysteries and humbugs of English commerce." As a metallurgist he might have remembered another: the use of the Cornish assay in the copper-trade. And impartiality might have led him to include under the head "humbug" the retention of Baumé's hydrometer in France and America, seeing that its scale exists in two, if not three different modifications, and that its indication cannot be converted into direct specific gravity by any simple calculation.

After discussing the materials for the process, the author gives a very full account of the reactions of the sodium hyposulphite solutions. Then follow the reactions of "extra solutions," apparently the double hyposulphite of sodium and copper.

The problem of extracting from auriferous silver ores a high percentage of both these precious metals by one process in the moist way the author admits is still awaiting its solution.

The amount of chemical operations requiring daily performance in the laboratory of lixiviation works is considerable. It includes pulp-assay of the ore and salt-mixture, determination of percentage of salt, calculation of value of ore from the two preceding data, pulp-assay of roasted ore and determination of soluble salts present, with calculation of value of roasted ore, assay of tailings, and lixiviation tests of roasted ore with ordinary and extra solutions. The execution of these different determinations is only partially laid down.

The second part of the book is devoted to the practical execution of the lixiviation process. The needful plant is fully described, with the addition of numerous illustrations, exceedingly well drawn.

A special chapter treats of the construction, price of erection, and working cost of a lixiviation works.

Mr. Stettefeldt's treatise may be decidedly recom-

mended to all metallurgists who have to deal with silver ores, though of course much of the information given is specially adapted to circumstances in the United States.

CORRESPONDENCE.

SHEEP DRESSING.

To the Editor of the Chemical News.

SIR,—This is the centre of large wool-producing districts, and many flock-masters use, for dressing sheep, solution of calcic sulphides, made on the spot by boiling sulphur in solution of lime, aiming to get the largest amount of sulphur dissolved by the smallest quantity of lime. The orange solution so made is complex—calcium sulphide of several degrees in sulphur and some hyposulphite is made. If alkali-makers who have large by-products of calcic sulphurets could see their way to make—*fit* for carriage, hard and dry, but soluble in water—a compound of sulphur and lime in which the sulphur was in excess, so as to approach the pentasulphurets, I think a good demand could be found for the same. It is troublesome to make in small quantitities with farmers' appliances, and will not keep in solution long when made. Such a form of sulphur would also find a use in treatment of vines and fruit trees, as the lime and sulphur solution is the best for treating them for insect and fungoid diseases, and is used by syringing. I am aware of recent improvements by which the former waste sulphides of the alkali-maker are now utilised, and sulphur regained. But possibly it might pay to use the sulphur compounds as above indicated, and I shall be glad to be placed in communication with anyone wishing further information, or who may see the way to supply the want here set before them, viz., a cheap form of calcium sulphide with excess of sulphur in form fit for export and soluble in water, to be used as dipping-bath for sheep, &c., against scab and allied diseases.—I am, &c.,

WM. ROE.

Graaff Rimel, Cape Colony, South Africa.

OBITUARY.

PROFESSOR CHEVREUL.

WE deeply regret having to put on record the death of Prof. E. Chevreul, the senior chemist of the world. Not, indeed, that we can be surprised at the demise of one who had earned a European reputation when our elderly *savants* were still in their cradles, or unborn; nor that anything in the shape of research and discovery could be expected from him, seeing that on August 31st next he would have reached the age of 103 years. But it is painful to see a link broken which connected us to the days of Lavoisier, Gay-Lussac, Berthollet, Davy, and Dalton. Much of the abundant and precious work of his long career is almost too well known to need recapitulation. But we may glance in passing at his wonderful researches on the fatty matters, fruitful alike theoretically and practically, and to his splendid investigations on colouring matters and on light, which for the first time gave the art of dyeing a rational foundation. The *doyen* of the students of France, as the deceased modestly called himself, closed his long and illustrious career on the 9th instant.

The Atomic Weight of Osmium.—Karl Seubert.—The author's experiments lead to the mean value 191·12 (O=15·96).—*Zeit. f. Anal. Chem.*, vol. xxviii., Part 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 12, March 25, 1889.

On Cobalt and Nickel Peroxides, and on the Volumetric Determination of these Metals.—Adolphe Carnot.—Inserted in full.

The Limits of Error which may be Committed in the Assay of Fine Gold.—Paul Charpentier.—The assay of fine gold, founded, on the one hand, upon the cupellation of this metal in presence of silver and lead, and on the other hand upon the treatment of the alloy with nitric acid, is capable of a very high degree of accuracy. In general the determination of gold by this method can be guaranteed to about 3-10,000ths. But this result can be reached only by adhering closely to certain experimental necessities which long practice has taught. The author has sought to determine what is the maximum error which may ensue if any one of these rules is neglected, whilst the others are adhered to. If the heat of the muffle is too high there may be a mean loss of gold of 24-10,000ths, and if it be too low an excess of 6-10,000ths. If the maximum quantity of lead has been used the mean loss is 2-10,000ths, and if it is too far reduced the mean excess may be 6-10,000ths. Both an excess and a deficiency of silver show an excess of gold, in the latter case to 100 per cent.

The Initial Phase of Electrolysis.—M. Piltschihoff.—The minimum of the electromotive force necessary to set up immediately a visible electrolysis does not, within certain limits, depend either on the nature of the salt or on the concentration of the solution. The minimum does not appreciably depend either on the combination-heat of the two metals nor on their electromotive force of contact, but essentially on the physical condition of the surface of the cathode.

The Electric Transfer of Dissolved Salts.—A. Chassy.—A salt of zinc in a mixture of copper and zinc salts is always transported in the direction of the current. If two salts, *e.g.*, sodium or barium nitrates whose weights are in a constant proportion, are placed in a mixture of any number of other salts the quantities of the two former salts transported will vary in absolute value, but their proportion will remain constant.

On Chloral Glycolalcoholate.—M. de Forcrand.

Determination of the Combustion-heats of Metaldehyd, of Erythrite, and of Tricarballylic Acid.—M. Louguinine.—These two thermo-chemical memoirs do not admit of useful abstraction.

Justus Liebig's Annalen der Chemie. Vol. ccl., Part 3.

Communications from the Chemical Laboratory of the Federal Polytechnicum at Zurich: Researches on the Azoles.—These communications comprise memoirs by A. Hantzsch on alkylised thiazoles from the thiamides; by G. Popp on thiazoles from amido-thiazoles; by H. Zürcher on the action of the metallic sulphocyanides and sulphurea upon chlorised acetacetic esters; and by G. Hofmann on seleno-cyanides and on selenazol compounds.

Researches in the Camphor Series (First Treatise).—E. Beckmann.—This very hypothetical paper does not admit of useful abstraction.

On the Three Isomeric Toluric Acids, and on the Behaviour of Metaxylol in the Organism.—A. Gleditsch and H. Moeller.—The three toluric acids form

crystals which melt only at high temperatures, and none of them agree with the liquid toluric acid of Schultzen and Naunyn. Metaxylol, if introduced into the organism of dogs, passes into the same crystallisable metatoluric acid which is obtained from glycocoll and metatoluylic acid.

Moniteur Scientifique, Quesneville.
4th Series, Vol. iii., April, 1889.

On Water Gas.—J. Lange and J. Lunge (*Zeitschrift für Angewandte Chemie*).—Even at 1000° the decomposition of watero vapour by carbon is incomplete. Before water-gas can be commonly used for heating or lighting, like coal-gas, a method must be found of communicating to this gas, which is in itself inodorous, a scent much more penetrating and persistent than that of coal-gas, since, by reason of the large proportion of carbon monoxide which it contains, it is at least five times more poisonous than coal-gas. The deadly character of a gaseous mixture seems to increase much more rapidly than the proportion of carbon monoxide. According to the researches of Dr. Wyss, the dangerous results of the inspiration either of coal-gas or water-gas are due solely to carbon monoxide. During the months of January and February, 1888, seven cases of poisoning from water-gas have occurred in New York. It is proposed that water-gas might be rendered odorous, so that its escape could be at once detected, by means of mercaptan.

Researches on Certain Compounds of Sulphur.—Dr. H. Rebs.—A memoir on hydrogen persulphide, the phosphorus sulphides, the barium ether-sulphates, and sulphuric anhydride.—From *Liebig's Annalen*.

Processes of Alkali Manufacture from a Thermo-Chemical and Electrolytical Point of View.—Dr. F. Hunter.—From the *Journal of the Society of Chemical Industry*.

Presence of Sugar in Cereals.—A. von Asboth.—The author shows that neither saccharose nor glucose is present in cereals. Earlier experimentalists have committed the error of inverting an aqueous or alcoholic extract of the grain by an acid. The author has shown that dextrine and analogous substances are dissolved in the water, or the alcohol is converted into sugar by acids.

Determination of Glycerin in the Lyes resulting from the Manufacture of Soap, and in Crude Glycerin.—Otto Hehner.—From the *Journal of the Society of Chemical Industry*.

On Cryolite, and its Substitution in the Glass Manufacture.—R. Zsigmondy (*Dingler's Journal*).—The price of cryolite having become too high for use in the preparation of opal-glasses, a substitute became necessary. C. Weinreb proposed sodium fluoride mixed with aluminous minerals. To obtain an alkaline fluoride he fused fluor-spar with potassium or sodium carbonate; the former of these compounds is too costly, but the latter appears to give satisfactory results. The author melts fluor-spar with potassium carbonate in presence of silica, lixiviates the mass obtained, and treats the concentrated boiling solution of potassium fluoride with a solution of sodium carbonate saturated at 38°. Potassium carbonate is precipitated and serves for a fresh operation. For determining combined hydrofluoric acid the author employs a modification of Knœffler's method for titrating sulphuric acid. He uses decinormal calcium chloride with phenolphthalein as indicator. The solution of potassium fluoride, containing potassium carbonate and silicate, is neutralised, hot, with hydrochloric acid after the addition of phenolphthalein, and treated with 1 c.c. of decinormal sodium carbonate, when the liquid turns red. An excess of the decinormal calcium chloride is then added until the red colour disappears. When all the potassium fluoride is decomposed the calcium chloride acts upon the sodium carbonate, the liquid becomes neutral and colourless. The excess of calcium chloride is then determined by Knœffler's method for the alkaline earths, *i.e.*, it is precipitated by a decinormal solution of sodium carbonate until the red colour reappears. It is then filtered, and the liquid is titrated with a decinormal solution of hydrochloric acid, after the addition of methyl-orange.

On Castor Oil.—K. Hazura and A. Grüssner (*Zeitschrift fur Angewandte Chemie*).—The authors infer from their experiments that the liquid acid of castor oil is not a single compound as it has been hitherto supposed, but a mixture of two isomeric acids of the composition $C_{18}H_{34}O_3$, one of which, ricinoleic acid, yields on oxidation trioxystearic acid, whilst the other, ricinisoleic acid, yields isotrioxystearic acid. The proportion of these acids is about 1 of the former to 2 of the latter. As no dioxystearic acid has been obtained from the oxidation of the liquid acids of castor oil it may be concluded that of all the fatty oils hitherto examined castor oil is the only one which contains no oleine.

On the Non-siccative Oils.—K. Hazura (*Zeitschrift fur Angewandte Chemie*).—All the non-siccative oils contain along with oleic acid, one or more non-saturated acids; probably linolic or linolenic acid.

On Gum Lac.—R. Benedikt, E. Ehrdich, and F Ulzer (*Zeitschrift fur Angewandte Chemie*).—Lac is a substance of the nature of the fats, and by successive oxidations with permanganate it is converted almost entirely into azelaïc acid and certain inferior fatty acids.

The Fat of Ucuhuba.—E. Valenta (*Zeitschrift fur Angewandte Chemie*).—This fat is of a yellowish brown, very consistent, of a peculiar aromatic odour, becoming disagreeable if heated. It is obtained from *Myristica surinamensis*. It contains about 10 per cent of oleic acid, the other ingredients being myristic acid, wax, resins, &c. It is an excellent material for the manufacture of candles.

Metallic Resinates for the Preservation of Wood.—M. Kretschmar (*Chemiker Zeitung*).—The timber is first immersed in a bath of a salt of copper or zinc and is then coated with an alkaline solution of resin.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 1.

Application of Electrolytic Conductivity in Quantitative Determinations.—E. Reichert.—This extensive memoir requires the four accompanying figures and diagrams. The author considers that the specific conductivity of a natural water is a characteristic and fundamental property which should not be omitted in any analysis.

The Examination of Spirit and Spirituous Liquors, Especially as Effected by Means of the Vapormeter.—J. Traube.—In this treatise the author discusses the capillarimetric method for the determination of fusel, the stalagmometric method, and the separation of impurities by means of saline solutions. He then examines the method of Röse for the determination of fusel and a vaporimetric method for determining the first runnings and the fusel, as well as the signification of the vaporimeter in the alcohol industry.

Determination of Raffinose in the Products of the Manufacture of Beet-Sugar—Prof. J. W. Gunning.—This paper does not admit of useful abstraction.

Quantitative Determination of Zinc along with Manganese.—G. Neumann.—The author, whilst studying the separation of zinc from other metals in a formic solution, met with an inaugural dissertation by Max Bragard, treating almost on the same subject. The author has reached the same conclusions as Bragard, and confirms his result that the determination of zinc in a formic solution in presence of iron and nickel is very useful. He

adds that under the same conditions a quantitative determination of zinc in the presence of manganese can be simply and rapidly effected.

A Source of Error in Determining the Nitrogen of Halogeniferous Bodies, and its Prevention.—Richard Zsigmondy.—In determining the nitrogen of such bodies meta-chlor-α-methyl-cinnamaldehyd-phenylhydrazon by the method of Dumas (using halogeniferous copper oxide and a plug of copper), the author obtained regularly from 1 to 2 per cent of nitrogen in excess. He traced the cause to the presence of chlorine in the copper oxide. He finds that this error may be avoided by passing carbon dioxide over the copper oxide whilst still in a state of ignition, and allowing it to cool in a current of the same gas.

Apparatus for the Electrolytic Determination of Metals.—Dr. L. C. Levoir.—This paper requires the accompanying figure.

The Presence of Arsenic in Bone Meal used for Feeding.—H. Fresenius.—"Feeding bone meal," so-called "precipitated phosphate" has been successfully added to the food of cattle in doses ranging from 2 to 15 grms. daily for young animals and 20 to 50 grms. for adult individuals. If the acid used in the manufacture is arseniferous, calcium arseniate or arsenite will accompany the phosphate. The proportion of arsenic in the samples examined ranged from 0·028 to 0·17 per cent (calculated as metallic arsenic).

Determination of Phosphoric Acid in Sweet Wines and on the Examination of Sweet Wines.—W. Fresenius.—The author recommends that the sugar present should be destroyed by fusion with soda and saltpetre.

Analyses of Pure Sherries.—E. Borgmann and W. Fresenius.—Not adapted for abstraction.

Absorptive Power of Grey Vulcanised Rubber.—G. Hüfner (*Annalen der Physik und Chemie*).—Within the temperatures 5° to 25° there is no defined coefficient of the absorption of atmospheric air. Between 15° and 25° no measurable quantities of nitrogen are absorbed by grey vulcanised rubber. The same quality absorbs its own volume of dry carbon dioxide at about −2°. The specific coefficient of absorption decreases with a rising temperature. The rubber is indifferent to hydrogen at temperatures from −2° to +13°. Even after the lapse of three months no absorption of gas could be detected.

Solubility of Certain Compounds of Gold.—Th. Rosenbladt (*Berichte Deutsch. Chem. Gesell.*).—The author has experimented with the aurochlorides of sodium, lithium, potassium, rubidium, and cæsium.

Determination of Pressure in Sealed Tubes.—A. Reychler.—The author's method cannot be described without the accompanying figure.

A Projection Saccharimeter.—Leon Laurent.—From the *Comptes Rendus*.

A New Refractometer.—C. Pulfrich.—This instrument consists of a rectangular prism of glass, to the horizontal surface of which is cemented a small glass cylinder for the reception of the liquid to be examined.

Determination of the Thermic Value of Coals.—W. Thomson.—From the *Journal of the Society of Chemical Industry*.

Apparatus for Determining the Fluidity of Lubricating Oils.—L. Barbey.—For the description of the apparatus we must refer to the original.

Areometer with Legible Thermometer Scale.—A. Gawalowski.—The thermometer scale is fixed above the areometer scale in the upper part of the instrument.

Determination of the Specific Gravity of Solids.—L. Brasse and E. Vlasto.—This description is imperfect without the figure.

An Improved Valve-burette.—G. Kroupa.—The valve is opened or closed by means of a glass rod secured to a screw with a fine thread.

A New Screw Pinch-Cock.—B. Proskauer.—This paper requires the accompanying figure.

A Modified Çalcimeter.—A. Bernard.—From the *Comptes Rendus*.

Modification of Soxhlet's Extraction Apparatus.—W. H. Kent, O. Grothe, and C. M. King.—From the *Journal of the American Chemical Society* and the Chemical News.

Tube for taking Samples of Fluid and Semi-fluid Substances from Casks.—A. Gawalowski.—The instrument consists in two concentric iron cylinders, closed below.

Purification of Mercury.—B. Karsten.—The author describes the method used in the physical laboratory at Kiel.

Development of Hydrogen in the Kipp Apparatus.—J. Habermann.—The author recommends the use of an alloy of tin and zinc.

The Reddening of Phenol.—A number of authors give a series of different explanations of this phenomena, and W. Hankó considers that possibly all may be right.

Production of Absolute Alcohol on the Small Scale.—J. Habermann.—The author places the lime used for dehydration not in the retort, but in a super-imposed appendage consisting of a cylinder tapering downwards, and inclosing a narrower cylinder of iron wire gauze, closed above,

The Application of Ammonium Dithiocarbaminate in Analysis.—Jos. Klein.—This paper will be inserted in full.

Determination of the Available Oxygen in the Peroxides by Means of Gaseous Hydrochloric Acid.—L. L. de Koninck and Ad. Lecrenier (*Zeitschrift fur angewandte Chemie*).—This paper requires the accompanying illustration.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Dr. Jean Paul Richter, Three Lectures on the Italian Renaissance Painters: their associations, their education, and their employments (with illustrations); Prof. E. Ray Lankester, Four Lectures on Some Recent Biological Discoveries; Mr. Eadweard Muybridge, of Pensylvania, Two Lectures on the Science of Animal Locomotion in its Relation to Design in Art (illustrated by the zoopraxiscope); Professor Dewar, Five Experimental Lectures on Chemical Affinity; Mr. Joseph Bennett, Four Lectures on the Origin and Development of Opera in England (with musical illustrations); Professor W. Knight, of St. Andrews, Three Lectures on I. The Classification of the Sciences, Historical and Critical; II. Idealism and Experience, in Philosophy and Literature; III. Idealism and Experience, in Art and Life (the Tyndall Lectures). The Friday Evening Meetings will be resumed on May 3rd, when a Discourse will be given by Sir Henry Roscoe, M.P., on Aluminium; succeeding Discourses will be given on May 10th, by Professor Dewar, on Optical Properties of Oxygen and Ozone; May 17th, by Professor Silvanus P. Thompson, on Optical Torque; May 24th, by the Rev. S. J. Perry, on the Solar Surface During the Last Ten Years; May 31st, by Professor Demetri Mendeleeff, on An Attempt to Apply to Chemistry One of Newton's Principles; June 7th, by Archibald Geikie, on Recent Researches into the Origin and Age of the Highlands of Scotland and the West of Ireland; and June 14th, by C. V. Boys, on Quartz Fibres.

MEETINGS FOR THE WEEK

Monday, 15th.—Medical, 8.30.
Tuesday, 16th.—Institute of Civil Engineers, 8.
—— Sanitary Institute, 8. "Sanitary Laws and Regulations Governing the Metropolis," by A. Wynter Blyth, M.R.C.S.
—— Pathological, 8.30.
Wednesday, 17th.—Geological, 8.
Thursday, 18th.—Chemical, 8. "Notes on Naphthalene Derivatives," by Dr. Armstrong and Messrs. Heller, Holding, Percival, Rossiter, and Wynne.

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NOTICE IS HEREBY GIVEN, That the next Half-yearly Examination for MATRICULATION in this University will commence on MONDAY, the 10th of June, 1889.—In addition to the Examination at the University, Provincial Examinations will be held at University College, Aberystwith; University College, Bangor; The Modern School, Bedford; Queen's College, Birmingham; University College, Bristol; University College, Cardiff; The Ladies' College, Cheltenham (*for Ladies only*); St. Gregory's College, Downside; New College, Eastbourne; The Heriot Watt College, Edinburgh; The Royal Medical College, Epsom; The Yorkshire College, Leeds; University College, Liverpool; The Owens College, Manchester; The School of Science and Art, Newcastle-on-Tyne; University College, Nottingham; The High School, Oswestry; Firth College, Sheffield; Stonyhurst College; and St. Cuthbert's College, Ushaw.

Every Candidate is required to apply to the Registrar (University of London, Burlington Gardens, London, W.) for a Form of Entry *not less than five weeks* before the commencement of the Examination.

Candidates are particularly requested to notice that the June Examination is, in the present and future years, to be held *a week earlier than heretofore.*

ARTHUR MILMAN, M.A., Registrar.

April 10th, 1889.

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THE CHEMICAL NEWS.

VOL. LIX. No. 1534.

ON THE LOSS OF VOLTAIC ENERGY OF ELECTROLYTES DURING CHEMICAL UNION.*

By G. GORE, LL.D., F.R.S.

IN this research the author has shown by suitable examples of measurement of the voltaic energy of different solutions by means of the "voltaic balance" (see *Roy. Soc. Proc.*, vol. xliv., pp. 151, 294, 300—308), the successive losses of energy which occur with every additional degree of complexity of a chemical compound. The following are some of the instances given :—

Energy.	Energy.	Energy.
I=3,310,985	Br=81,022,500	Cl = 1,282,000,000
KI = 16,361	KBr = 66,909	KCl = 699,803
KIO_3 = 468	$KBrO_3$ = 364	$KClO_3$ = 239
		+KCl = 53
		+$Am_2C_2O_4$ = 28·4

	Energy.
KCl	699,803
NaCl	207,589
„ +KCl	5,959
K_2SO_4	2,274
Na_2SO_4	2,020
+K_2SO_4	112
+2NaCl.KCl	41
+4K_2CrO_4..	−225
+8K_2CO_3	−11435

In all the cases every addition to the degree of complexity of the definite compounds formed was attended by a large decrease of voltaic energy, and the relative amount of electro-negative energy varied inversely with the degree of molecular complexity of the substance.

ON COBALT AND NICKEL PEROXIDES, AND ON THE VOLUMETRIC DETERMINATION OF THESE METALS.

By ADOLPHE CARNOT.

IT is known that the action of potassa, conjointly with that of chlorine, bromine, iodine, or of an alkaline hypochlorite, gives in solutions of cobalt or nickel black precipitates absolutely similar in appearance, though M. Herrenschmidt has remarked that cobalt peroxide thus obtained presents a brown tint, whilst the tint of nickel remains black if examined under the microscope.

If the precipitation is effected by means of oxygenated water and potassa we obtain with nickel a green precipitate of hydrated protoxide, just as with potassa alone. Cobalt yields a precipitate of a rather light brown, easy to distinguish at sight from the foregoing peroxides.

Being struck with this difference of aspect the author has made a series of experiments to demonstrate the state of oxidation of the metals in these precipitates. This examination presented the greater interest from an analytical point of view, as almost all the text-books recommend a volumetric process (Fleischer's method) founded on the uniformity of the composition of the precipitates obtained with nickel and cobalt by the use of potassa and bromine, or a hypochlorite.

The first results obtained were not in harmony with this view, and it was therefore necessary to renew and to vary the experiments.

After the addition of the oxidising agent and of the potassa the liquid was kept at a boil for some time, and then left to settle; the deposit was washed with pure or alkaline water, first by decantation and then on the filter, or an account was taken of the liquid left with the precipitate on submitting to the same experiment an equal volume of the last liquor decanted.

The weight of the metal taken for the experiment is known beforehand, according to the volume of the standard solution employed. The proportion of disposable oxygen (over and above that of the protoxide) was determined by pouring into the flask containing the washed precipitate an excess of potassium iodide and then rather dilute hydrochloric acid, leaving the solution to be completed in the cold, then determining the free iodine by means of a decinormal solution of sodium thiosulphate, added until the liquid is decolourised, and finally adding starch and running in a centinormal solution of iodine until a blue colour appears. The trials with ferrous sulphate, or oxalic acid, or potassium permanganate in a sulphuric solution are less accurate because the rose colour due to the cobalt prevents that of the permanganate from being distinctly seen.

The results of these experiments may be thus summed up :—

The brown oxide obtained on precipitating cobalt by oxygenated water and potassa at a boil, presents the exact composition of a sesquioxide, Co_2O_3.

The black oxide of nickel, precipitated by hypochlorite or by bromine with potassa, corresponds also exactly to the formula of the sesquioxide, Ni_2O_3.

The oxide of cobalt, nearly black, obtained by the use of hypochlorite, of bromine, or iodine, always contains a proportion of oxygen decidedly greater than that which corresponds to the sesquioxide. In place of $Co_{10}O_{15}$, *e.g.*, experiment gives as a mean $Co_{10}O_{16}$ with hypochlorite, and $Co_{10}O_{16\cdot25}$ with bromine or iodine. If we remark on the one hand that the washings have been effected with care so as not to leave any excess of the oxidising reagent, and on the other hand that the black precipitate appears really to differ from the brown precipitate formed by oxygenated water, we are led to think that there is formed under these conditions a saline compound containing a little cobalt dioxide along with sesquioxide. The composition of the precipitate given by hypochlorite may be represented by the formula $2CoCo_{2,4}Co_2O_3$; that of the precipitate obtained by means of bromine or iodine would correspond to $2CoO_{2,3}Co_2O_3$.

From an analytical point of view it is certain that we commit an error if we regard these precipitates as sesquioxides. In place of reckoning for one equivalent of available oxygen two equivalents of cobalt, we can only reckon 1·67 with the hypochlorite and 1·60 with bromine.

Nickel, on the contrary, may be very well determined volumetrically after the use of these same reagents by the method indicated above.

The determination of cobalt can also be effected accurately, but on condition of using as reagents oxygenated water and potassa. The operation is even easier than in the former case, because the excess of the oxidising agent disappears during the ebullition, which is not the case with the other reagents. If the two metals occur together we can determine the cobalt singly with accuracy by the use of oxygenated water and potassa, since the nickel is not peroxidised. Several synthetic experiments have given identical results for the same quantity of cobalt, whether in the presence or the absence of nickel. The author has also proved that boiling with ammonia in order to destroy the nickel peroxide, if any was formed, does not modify the final result.—*Comptes Rendus.*

* Abstract of a Paper read before the Birmingham Philosophical Society.

ON SOME ATTEMPTS TO PREPARE THE OXY-HALOID DERIVATIVES OF CHROMIUM, WITH ESPECIAL REFERENCE TO THE OXY-CYANIDE.

By S. G. RAWSON, B.Sc.

In the *Philosophical Magazine*, xii., 322, there is a paper by Girard on the preparation of the oxy-iodide of chromium, the results of which seemed to me to warrant further investigation. The product which he obtained was not analysed, but it was assumed to contain chromium, and various properties of the body are given. I have repeated his experiments, using the proportions given by him, but could obtain no compound giving any chromium. I then endeavoured to prepare the corresponding oxy-bromide and oxy-cyanide, and though I did not succeed in isolating the latter body, yet I think I obtained proof of its formation in small quantities. In all probability many attempts will have been made to prepare these bodies, but there seems to be no record of the failures, and hence it may happen that in each fresh attempt many of the old failures are repeated. From this point of view, therefore, it is, that I give briefly my own experiments in this direction.

The body obtained by Girard was described by him as a deep red oily liquid which boiled at 149° C., giving off a dense red vapour, corroded and blackened paper and wood, and imparted a deep brownish red stain to the skin, and which was prepared by the distillation of sulphuric acid with potassium bichromate and potassium iodide. I repeated his experiment, taking exactly the proportions given by him, and did obtain very small quantities of a deep red liquid, but in which I was unable to detect a trace of chromium. In a second experiment a trace was found, but so slight, not exceeding 0·00046 grm., that it probably arose from a little of the finely-divided bichromate which had been mechanically carried over. I determined the amount of chromium present by comparison with standard borax beads, *i.e.*, those containing the same amount of borax and a varying but known amount of chromium until a bead of the same depth of tint was obtained. Incidentally I may mention that I found that 0·000005 grm. chromium colours the bead of a recognisable green tinge, but it must be compared with a bead of pure borax. The red liquid consisted of hydriodic acid, very strongly coloured with free iodine, accompanied by traces of sulphurous and sulphuric acids. It behaved in all respects as Girard stated, with the one exception that it distilled at about 129° (the boiling-point of hydriodic acid) instead of 149° C. I also prepared a strong solution of hydriodic acid with much free iodine dissolved in it; this behaved similarly in all respects, and distilled at 129° C. Giraud used the normal potassic chromate, and in my experiments I used both this salt and also the bichromate.

Having convinced myself that the oxyiodide could not be obtained in this way I tried various other methods for its preparation. I passed the vapour of CrO_2Cl_2 in a current of carefully dried CO_2 over the surface of ethyl iodide. This became at once of a reddish brown colour, which gradually deepened, and finally a reddish precipitate was formed; the whole was then heated, the current of CO_2 still passing. A purplish liquid distilled over, leaving behind in the flask the red precipitate. On analysis the distillate was found to contain ethyl chloride, iodide, and free iodine, whilst the residue consisted of a mixture of iodine and Cr_3O_4.

Owing to the constant separation of iodine in this experiment, it seemed as though the presence of a diluent would be beneficial. The best one I found to be CS_2, the use of such reagents as ether or alcohol being of course precluded in the presence of the oxychloride. In the first experiment made a violent ebullition took place, and part of the contents were ejected from the flask, for, depending on the presence of the carbon disulphide, both the ethyl iodide and the chromium oxychloride were mixed together in considerable quantities. A heavy precipitate formed at the same time. With a large excess of CS_2 the reaction was much less violent, but the precipitate again formed, and was merely a mixture of I and Cr_3O_4. I did not analyse this yellow precipitate, but assumed that it was the yellow oxide of chromium. The liquid was carbon disulphide, containing a large quantity of iodine in solution. I then tried the direct action of fuming hydriodic acid on chromic acid in the presence of solid $ZnCl_2$, but iodine alone separated, with evolution of much heat. A mixture of potassic iodide, chromic acid, and solid zinc chloride was treated with (1) HCl, (2) CH_3COOH, (3) H_2SiF_6, but in all cases, sooner or later, iodine was set free as such. Chromium oxychloride was then heated with calcium iodide in a sealed tube at 140° C. for six hours. On cooling, the tube was cut up and a part of the material was carefully heated in a current of dry CO_2 gas. At first much undecomposed CrO_2Cl_2 came over, and then iodine, leaving behind chromium oxide and a mixture of $CaCl_2$ and CaI_2. The experiment was repeated at a temperature of 125° C. for three hours. In this case, however, much of the CrO_2Cl_2 remained unacted upon. Finally, the action of the oxychloride on silver iodide was tried, the mixture being heated between 100° and 110° C. for nine hours, but the result was similar. On taking some of the residue, however, and cautiously warming it in a closed dry test-tube, beautiful crystals of what I believe to be ICl_3 were obtained, some of them nearly half an inch in length.

In the case of the oxybromide, a mixture of the bromide and bichromate of potassium was treated with sulphuric acid, but nothing but free bromine distilled over. Chromium oxychloride was also heated with calcium bromide in sealed tubes at varying temperatures during varying times, but the results were the same as those obtained in the case of the iodide. In every case the oxychloride is decomposed, but the iodine or bromine does not take the place of the chlorine, but remains in the free state, the chromium becoming converted into an oxide. Another difficulty in the sealed tube experiments lies in the fact that at high temperatures the oxychloride is converted into the trichromyl chloride, whilst at low temperatures very much of it is left unacted upon.

Finally, I endeavoured to prepare the oxycyanide, and though I was unable to isolate it, yet, as previously mentioned, I think I obtained some proof of its formation in small quantities. The first and most obvious method was to treat a mixture of potassic cyanide and potassic bichromate with sulphuric acid, when a violent reaction ensued, but only hydrocyanic acid was produced. On the first addition of the sulphuric acid a small portion of the mass took fire spontaneously and burned for a moment. Hence, owing to the violence of the decomposition, I thought that bettter results might perhaps be obtained if the mixture were kept cool. The next experiment was therefore performed at a temperature of −10° C., but still only hydrocyanic acid was given off. Another attempt with the sulphuric acid slightly diluted also failed. Some pure dry mercuric cyanide was then placed in a porcelain boat and warmed and the vapour of CrO_2Cl_2 in a current of dry CO_2 was passed over it. A little of the oxychloride passed over unchanged, together with a trace of mercuric cyanide, and then the whole mass in the tube glowed with a vivid incandescence and complete decomposition took place. A portion of the residue was then exhausted with ether, but in this extract mercury was found, and hence might itself have been present as the cyanide. Another portion, treated with carbon disulphide, left no residue on evaporation. Some of the oxychloride was then heated with mercuric cyanide in a sealed tube for four hours at 135° C., and as there seemed to be no appreciable change at the end of that time the temperature was raised to 190° for another hour and a half. On

cooling there seemed to be a very few reddish yellow crystals, A part of the tube was then exhausted by a Sprengel pump to remove the undecomposed CrO_2Cl_2, and then treated with carbon disulphide and again with ether. In the former solution nothing was found, and in the latter much mercury, chromium, and cyanide, so that again the cyanogen might have been present as the mercury salt. Another portion was then treated successively with CS_2, ether, and alcohol. The alcoholic extract, which was of a deep red colour, was distilled, but very soon the liquid became quite colourless, and a gelatinous precipitate of a yellowish brown colour formed, probably chromium oxide. Another tube was then prepared and the previous treatment repeated.

I had hoped that if, on distilling the alcoholic extract, cyanide was found in the distillate, it might be inferred that some or all of the substance which dissolved in the alcohol was oxycyanide; but though the distillate did give distinct cyanide reactions, yet, when mercuric cyanide dissolved in alcohol is distilled, cyanide is also found in the distillate, and hence the presence of cyanogen under these circumstances could afford no definite proof. I then tried heating silver cyanide with the oxychloride in a sealed tube for six hours at 130°. On cutting up the tube as soon as the mass was exposed to the air a portion at once took fire. The residue was, however, submitted to the same treatment as before. The alcoholic extract was at first deep red in colour, but it rapidly became brownish red, and there was much silver cyanide held in suspension. So fine was the state of division of the silver salt that I found it impossible to filter it off, and though, on adding $(NH_4)_2S$ and filtering, much cyanide was present, yet, if silver cyanide be suspended in water and treated with $(NH_4)_2S$, decomposition also takes place and cyanide can be readily detected in the filtrate. Some of the residue was then heated in a current of pure dry CO_2 and the gas passed into water, which gave very distinct cyanide reactions, whilst AgCy similarly treated, in fact heated until it actually melted, gave none or hardly any. Chromium was also present in the aqueous solution, and as the residue, before being heated in CO_2, had been already exhausted in the pump and the residual chromium oxychloride thus removed, I cannot but think that a small quantity of the oxycyanide had been produced.

It will have been noticed that in every case the ethereal and alcoholic extracts were tinged more or less of a red colour, and this was so well marked that I endeavoured to discover the reason. I prepared some trichromyl chloride and found that this was hardly soluble in carbon disulphide, but dissolved much more easily in ether and in alcohol, the solutions becoming red. In the formation of trichromyl chloride, however, chlorine is produced, and it might be urged that the chlorine thus set free reacted on the silver cyanide, forming silver chloride and cyanogen, and that it was this cyanogen which I had detected. But I do not think that this can be so, because in the first place, on opening the tube, most of the cyanogen would certainly escape in the gaseous state; and again, as the residue was exhausted, this would remove the residual gas. I repeated the experiment, however, in a different manner. In the first place, chromium oxychloride was again heated in a closed tube with mercuric cyanide for fifteen hours at 124° C., this being just about the boiling-point of the oxychloride. The tube was then opened and the residue extracted with carbon disulphide. On shaking the disulphide with water the aqueous extract gave the cyanide reactions, but there was not a trace of mercury. Chromium was also present, but there was much undecomposed oxychloride, and hence some, at any rate, of the chromium will have arisen from this source, but these results would also tend to show that a little oxycyanide must have been formed. I then heated the oxychloride with silver cyanide in a flask furnished with an inverted condenser, the joint between the flask and the condenser being made tight with asbestos and gypsum, and to the free open end of the condenser was attached a calcic chloride drying tube. The whole was then heated to 120° C. for sixteen hours and kept in a dark place. At the end of that time there was a dark grey-coloured residue, and on warming a little of this in a test-tube it suddenly glowed, leaving behind a greenish mass of Cr_2O_3. There did not seem to be anything dissolved out by carbon disulphide, but an alcoholic extract contained much cyanide. This, as already mentioned, was due, at any rate in great part, to the difficulty of filtering off all the silver cyanide, which as I have shown, is easily decomposed by ammonium sulphide. I then treated mercuric cyanide with the oxychloride in a similar manner, keeping at a temperature of about 124° for eight to ten hours. A part was then treated with CS_2 without previous exhaustion in the Sprengel pump, and in this was much cyanide as well as chloride and chromium, but there was not a trace of mercury, and so once more it would seem as though the oxycyanide was present. The cyanogen was not present as gaseous cyanogen chloride, for this being a volatile substance, would have escaped through the calcium chloride drying tube. The method employed did not lend itself either to the supposition that solid cyanogen chloride had been produced. I then tried to separate the cyanide from the oxychloride by placing some of the material in a porcelain boat and passing over it carefully dried CO_2, whilst the tube was at the same time cautiously heated, the products being passed into water. In the aqueous solution both cyanide and chloride occurred, and hence this kind of fractional volatilisation did not effect the separation. As a last resource I placed some of the mixture in a fractionating flask, hoping to first volatilise the oxychloride and then perhaps some of the oxycyanide would either distil or sublime, but on applying a very moderade heat the whole exploded with great violence, the material being flung in a blazing condition in all directions. Hence, though it seems from various indications as though the oxycyanide had been prepared, yet no method which I have been able to devise has proved effectual in separating it from the other bodies occurring with it.

I may add in conclusion that I found the reaction with $(NH_4)_2S$ and the subsequent addition of Fe_2Cl_6 by far the best method for the detection of a cyanide. In some cases I was unable to detect any cyanide at all with the ferrocyanide tests, whilst the sulphocyanide gave it at once. In all cases where the oxychloride had to be dissolved out I was obliged to use CS_2, this being the only substance which was not acted upon by the oxychloride, at any rate not at once, and it has, moreover, the advantage of not dissolving a trace of $HgCy_2$, which latter body dissolves with considerable ease in both absolute alcohol and ether.

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ON THE

CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

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Various experiments, attended with but little or no success, have been made by distinguished chemists at different periods of time to convert benzol-phenol into aniline.

Some years since, Professor V. Merz and W. Weith† obtained aniline, together with diphenylamine, by heating benzol-phenol and zinc-ammonium chloride at a temperature of 280—300°. Later experiments, made in the laboratory of Professor Merz,‡ have shown that the above-mentioned

* "University Studies, Published by the University of Nebraska," October, 1888.

† *Berichte der Deutschen Chem. Gesellschaft*, xiii., 1298.

‡ P. Müller: "Inaugural-Dissertation." Aarau, 1886.

changes take place more readily when ammonium chloride is added to the zinc-ammonium chloride and the temperature raised to 330°. Under these conditions the three cresols have been converted into the corresponding mono- and ditolylamines, as well as the xylenes into primary and secondary amines. It has been further proved that zinc-ammonium bromide and ammonium bromide produce similar results to those given by zinc-ammonium chloride and ammonium chloride.

In order to ascertain whether the above reactions are common to the benzol series or not, I have undertaken the conversion of some of the higher homologues of benzol-phenol into primary and secondary amines with the following results:—

Isobutylphenol.

Isobutylphenol, prepared by the method given by Liebmann,* boiling at 230°, was heated in closed tubes with zinc-ammonium bromide and ammonium bromide in the proportions by weight of 1 : 3 : 1 for forty hours at a temperature of 320°—330°.

The tube-contents showed indistinct layers: the upper, an amorphous mass of a dark green colour; the under layer, a semi-solid mass of a light green colour, containing an abundance of darker particles. Accompanying these was a quantity of a dark green oily liquid. During the reaction water was formed in abundance in the tubes.

The opening of the tubes showed considerable pressure. The escaping gas possessed an aromatic odour, and burned with a feeble flame.

The tubes were further heated during six hours at the same temperature; the contents showed no special change from the appearances above described, but the oily portions were *darker in colour, and the layers* not so distinctly marked. The treatment of the tube-contents was as follows, and this method, essentially the same as that used by Merz and Müller† for the separation and quantitative estimation of monophenyl and diphenylamine, and unchanged phenol from benzol-phenol, was followed in subsequent experiments with other phenols. The reactions-mass was warmed with dilute hydrochloric acid until complete solution took place, with the exception of floating charred particles. Floating on the surface of the green-coloured solution was a dark brown oil. To insure complete separation of the substances, the entire solution was warmed with ether under reversed condenser. The oil dissolved readily in the ether. The primary base was sought for in the acid solution, and the secondary base and unchanged phenol in the ether extract.

The addition of an excess of ammonia to the acid solution caused the separation of a light brown oil, which after extraction with ether and drying over caustic potash was fractionally distilled and weighed.

Phenisobutylamine:—

$$N\begin{cases}C_6H_4.C_4H_9\\H\\H\end{cases} = C_{10}H_{13}.NH_2.$$

The larger part of the primary base—a light brown oil—had a constant boiling-point of 230°—231°. The amidoisobutylamine obtained by Studer‡ from aniline, hydrochloric acid, and isobutyl-alcohol, boiled at the same temperature. The acetyl compound of phenisobutylamine crystallised from warm alcohol in satiny leaflets, which melted at 170°, corresponding in all respects with the amine of Studer. According to the investigations of Pahl§, it seems evident that Studer's base is a *p*-amidoisobutylamine.

The ether extract, separated from the acid solution by means of a separation funnel, was filtered to remove charred particles (which particles were dried and weighed), then thoroughly shaken with sodium hydrate to free the sought-for secondary amine from any unchanged phenol which might be present.

Diphenisobutylamine;—

$$N\begin{cases}C_6H_4.C_4H_9\\C_6H_4.C_4H_9\\H\end{cases} = C_{20}H_{26}NH.$$

The so-isolated secondary amine—a thick oily liquid of a deep brown colour—was twice distilled with superheated steam. By this means a light golden oil was obtained, which became colourless after distillation in an atmosphere of hydrogen. A small portion distilled over at 290°—305°, a greater amount between 305°—315°; at 315° partial decomposition took place, yellowish white fumes were given off. (Under similar conditions diphenylamine boiled at 297°).

An analysis of the portion distilling between 305°—315° gave the following result:—

I. 0·2176 grm. substance gave 0·6793 grm. carbon dioxide and 0·183 grm. water, corresponding to 0·18525 grm. C. and 0·02033 grm. H.

II. 0·1642 grm. substance gave 8 c.c. of moist nitrogen (thermometer 20° C., barometer 760 m.m.) equal to 0·0090632 grm. N.

III. 0·2737 grm. substance gave 13 c.c. of moist nitrogen (thermometer 21° C., barometer 726 m.m.) equal to 0·0141219 grm. N.

Calculated for $C_{20}H_{27}N$.		Found. I.		Found. II.
	Per cent.	Per cent.		Per cent.
C_{20} = 240	85·41	85·13		—
H_{27} = 27	9·61	9·34		—
N = 14	4·98	5·51		5·51
281	100·00			

I was unable to obtain the base other than as a thick oil even at temperature of −15° C. A drop of nitric acid added to the light yellow-brown solution of diphenisobutylamine in concentrated sulphuric acid produced a violet tint, which changed rapidly to blue and then to blue-black.

Finally, the unchanged phenol separated from the first ether extract was again set free by hydrochloric acid, isolated with ether, and distilled at 229°—233°. The investigations proved that in its qualitative aspects, at least isobutylphenol is analogous to benzol-phenol, the cresols, and the xylenes. The results of repeated experiments have shown that a better yield of primary and secondary amines is obtained by the action of zinc-ammonium bromide than with zinc-ammonium chloride. With each were used twenty grms. of phenol, sixty grms. of the bromide or chloride of zinc and ammonium, and twenty grms. of ammonium bromide or chloride, and the temperature was maintained at 320°—330° for forty hours.

Isobutylphenol.	Zinc-ammonium bromide. I.	II.	III.	Zinc-ammonium chloride. I.	II.	III.	
Phenisobutylamine ..	30	34	35	20	30	28	p. c.
Diphenisobutylamine.	25	20	22·5	19	20	18	„
Unchanged phenol ..	38	40	36·5	45	44·5	44	„
Carbonised substance.	2	1	1·6	2	2·1	3·9	„

Derivatives of Diphenisobutylamine.

The platinum double salt—$(C_{20}H_{26}NH.HCl)_2Pt.Cl_4$—was most readily obtained by adding to an alcoholic solution of the hydrochloric acid salt an alcoholic solution of platinum chloride. An oily salt separated at first, which after standing changed to a granular golden-brown mass.

The mass was with difficulty soluble in water, but dissolved readily in hot alcohol, from which it crystallised in golden needles. The twice crystallised salt was dried over sulphuric acid in vacuum and at 110°, then analysed with the following result:—

I. 0·3300 grm. of the salt gave 0·0670 grm. platinum.
II. 0·3539 „ „ 0·0713 „ „

* *Berichte der Deutschen chem. Gesellschaft*, xiv., 1842.
† *Ibid.*, xix., 2902.
‡ Studer, *Annalen*, 211, 236.
§ *Berichte der Deutschen chem. Gesellschaft*, xvii., 1233.

Calculated for $C_{20}H_{29}NH.HCl)_2PtCl_4$.	Found. I.	II.
20·01 per cent Pt ..	20·30 ..	20·14 per cent Pt

Acetyldiphenisobutylamine:—

$$N\begin{cases}C_6H_4.C_4H_9\\C_6H_4.C_4H_9\\C_2H_3O\end{cases}=C_{22}H_{29}NO.$$

To form this compound, diphenisobutylamine was heated with an excess of acetic anhydride for two hours at a temperature of 130°. The fluid darkened in colour, and upon neutralisation of the free acid with sodium carbonate, a thick crystalline mass of a grey-white colour separated. This mass was thoroughly washed, dried, and crystallised out of benzol by addition of a small quantity of absolute alcohol in glistening white leaflets with 75° as the constant melting-point. The crystals dissolved with difficulty in hot water, readily in alcohol and benzol. Efforts to obtain the base from this compound by heating with sodium carbonate and caustic soda were unsuccessful, the acetyl compound remaining undecomposed. The analysis gave the following result:—

0·2895 grm. substance gave 0·2383 water, corresponding to 0·02647 H, and 0·8640 grm. carbon dioxide to 0·23565 grm. C.

Calculated for $C_{22}H_{29}NO$.			Found.
C_{22}	264	81·73 per cent	81·39 per cent
H_{29}	29	8·98 ,,	9·14 ,,
N	14	4·34 ,,	— ,,
O	16	4·95 ,,	— ,,
	323	100·00 per cent	

Isoamylphenol.

The isoamylphenol, which formed the starting-point of the following experiments, was made after the method given by Liebmann, and distilled at 240°. The experiments were conducted similarly to those with isobutylphenol. With every 20 grms. of phenol sixty grms. of zinc-ammonium bromide and twenty grms. of ammonium bromide were used. The substances were heated in closed tubes for forty hours at a temperature of 330° to 340°. On opening the tubes a very disagreeable-smelling gas escaped, which burned with a feeble flame for a few seconds. The tube-contents were in general appearance similar to those already described. Water was formed in abundance, and the reaction-mass was dark green in colour. The bases were separated by the method used with isobutylphenol.

Phenisamylamine:—

$$N\begin{cases}C_6H_4.C_5H_{11}\\H\\H\end{cases}=C_{11}H_{15}.NH_2,$$

a dark brown oil of weak basic character boiled at 259° to 262°. The distillation was continued until the temperature had reached 266°, when only a small amount of carbonised substance remained. It seems probable that the oil distilling between 259°—262° is identical with the amido-amyl benzol prepared by Calm,* by the action of chlor-zinc aniline upon fermentation amylic alcohol, of which the boiling-point is given at 256°—258°. It gave upon analysis the following results:—

0·1547 grm. substance gave 0·4566 grm. carbon dioxide and 0·1415 grm. water, equal to 0·12453 grm. C. and 0·01572 grm. H.

Calculated for $C_{11}H_{17}N$.			Found.
C_{11}	132	80·98 per cent	80·50 per cent
H_{17}	17	10·43 ,,	10·16 ,,
N	14	8·59 ,,	—
	163	100·00 ,,	

* *Berichte der Deutschen chem. Gesellschaft*, xv., 1643.

Diphenisamylamine:—

$$N\begin{cases}C_6H_4.C_5H_{11}\\C_6H_4.C_5H_{11}\\H\end{cases}=C_{22}H_{30}NH$$

was obtain as a thick dark brown oil, which boiled at 301° to 325°. In order to purify it, it was twice distilled with super-heated steam, then in an atmosphere of hydrogen, when an almost colourless oil distilled over between 319° to 321°.

The analysis confirmed the presence of a secondary amine:—

I. 0·2529 grm. substance gave 0·7925 grm. carbon dioxide and 0·2350 grm. water, equal to 0·21613 grm. C. and 0·02611 grm. H.

II. 0·2291 grm. substance gave 10 c.c. of moist nitrogen (thermometer 22° C., barometer 729 m.m.) equal to 0·010854 grm. N.

Calculated for $C_{22}H_{31}N$.			Found.
C_{22}	264	85·44 per cent ..	85·45 per cent
H_{31}	31	10·03 ,, ..	10·32 ,,
N	14	4·53 ,, ..	4·73 ,,
	309	100·00 ,,	

Upon standing, the amine became darker in colour, and in concentrated sulphuric acid dissolved with an exquisite golden colour, which grew darker in the air; the addition of a nitrite or of nitric acid to this solution changed the colour, first to light violet, then to a deep blue. In connection with these bases, a considerable quantity of unchanged phenol was found, which was isolated and distilled. Boiling-point 247°—250°.

The results of corresponding experiments with the bromides and chlorides of zinc and ammonium are here tabulated. Temperature, 330°—340°; time, forty hours.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.			
Isoamylphenol.	I.	II.	III.	I.	II.	III.	
Phenisamylamine ..	35	38	31	25	35	33·2	p.c.
Diphenisamylamine	21	20	25	17·4	19·1	18	,,
Unchanged phenol..	36	37	35·7	40	32	39·3	,,
Carbonised substance	1	0·5	0·8	3	2·8	4	,,

Derivatives of Phenisamylamine.

The platinum double salt—$(C_{11}H_{17}N.HCl)_2PtCl_4$—separated as a canary-coloured amorphous mass when to a hydrochloric acid solution of the base platinum chloride was added in slight excess. The amorphous floating-mass was dissolved with difficulty in hot water, more readily in hot alcohol, and was crystallised from a hot mixture of the two in beautiful golden needles.

For the analysis, it was dried at 100°—110°, when it gave the following result:—

0·3464 grm. of the salt gave 0·0912 grm. platinum.

Calculated for $(C_{11}H_{17}N.HCl)_2PtCl_4$.	Found.
26·43 per cent Pt	26·33 per cent Pt.

Benzoylphenisamylamine:—

$$N\begin{cases}C_6H_4.C_5H_{11}\\C_7H_5.O\\H\end{cases}=C_{18}H_{21}NO.$$

Phenisamylamine was treated with an excess of chlor-benzoyl, and the reaction which commenced at once was fully completed in an hour. During the operation a light brown crystalline mass separated, which was thoroughly washed, made neutral with sodium carbonate, and crystallised from hot absolute alcohol. After a second crystallisation, exquisite crystals of a leaf-like form and a mother-of-pearl lustre shot out from the solution in great abundance. These crystals, which dissolved readily in hot alcohol, and in cold chloroform and benzol, had a constant melting-point of 148·5°. Calm* gives the melting-point of the benzoyl compound of his amido-amyl-benzol at 146°—149°.

* *Berichte der Deutschen chem. Gesellschaft*, xv., 1645.

The analysis resulted as follows:—

0·2060 grm. substance gave 0·6101 grm. carbon dioxide and 0·1452 grm. water, equal to 0·16638 grm. C. and 0·01613 grm. H.

Calculated for $C_{18}H_{21}NO$.			Found.
C_{18} – 216 –	80·89 per cent	..	80·76 per cent
H_{21} – 21 –	7·87 ,,	..	7·83 ,,
N – 14 –	5·25 ,,	..	—
O – 16 –	5·99 ,,	..	—
267 –	100·00 ,,		

Derivatives of Diphenisamylamine.

The platinum double salt—$(C_{22}H_{30}NH.HCl)_2PtCl_4$.

The salt was best prepared by conducting dry hydrochloric acid gas into an ether solution of the base. The ether was evaporated and an oily compound obtained, which dissolved readily in absolute alcohol.

The addition of an alcoholic solution of platinum chloride to this solution, gave, after some days' standing, a compact, dark golden, slightly crystalline body, which difficultly soluble in hot alcohol. After thorough washing with water it was dried over sulphuric acid, and finally at 100°—110°.

The analyses were as follows:—

I. 0·2416 grm. substance gave 0·04450 grm. platinum.
II. 0·3396 ,, ,, ,, 0·06384 ,, ,,

Calculated for $(C_{22}H_{30}NH.HCl)_2PtCl_4$.	Found. I.	II.
18·92 per cent Pt	18·41	18·76 per cent Pt

Acetyldiphenisamylamine:—

$$N\begin{cases} C_6H_4.C_5H_{11} \\ C_6H_4.C_5H_{11} \\ C_2H_3O \end{cases} = C_{24}H_{33}NO.$$

In the preparation of this substance one molecule of the base was heated with two molecules of acetic anhydride for four hours at a temperature of 130°.

The chocolate-brown resulting-mass became greyish white after a thorough washing with water and neutralisation of the free acetic anhydride. It was crystallised from hot benzol in shining white leaflets, which melted at 81°, dissolved readily in warm benzol and chloroform, also in hot absolute alcohol.

The analysis gave the following result:—

0·1348 grm. substance gave 0·4056 grm. carbon dioxide and 0·1172 grm. water, corresponding to 0·1104 grm. C. and 0·01302 grm. H.

Calculated for $C_{24}H_{33}NO$.			Found.
C_{24} – 288 –	82·05 per cent	..	81·89 per cent
H_{33} – 33 –	9·40 ,,	..	9·65 ,,
N – 14 –	3·98 ,,	..	— ,,
O – 16 –	4·57 ,,	..	— ,,
351 –	100·00 per cent.		

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1889.

Mr. WILLIAM CROOKES, F.R.S., President, in the Chair.

(Concluded from p. 177).

31. "*The Determination of the Constitution of the Heteronucleal αβ- and ββ di-derivatives of Naphthalene.*" (Second Notice). By HENRY E. ARMSTRONG and W. P. WYNNE.

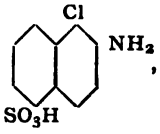
This communication is a continuation of that brought under the notice of the Society at the previous mention (*cf. Chem. Soc. Proc.*, 1889, No. 64, pp. 34—37), and is an account of the constitution of the three isomeric sulphonic acids prepared from 1 : 2 α-chloro-β-naphthylamine in the manner described in the former notice.

In displacing the NH_2 radicle of the amidochlorosulphonic acids by v. Baeyer's hydrazine method (*cf.* Haller, *Ber.*, 1885, 90), the authors were for some time seriously misled, as the products obtained were impure, owing to the extreme sensitiveness of the hydrazines to the action of hydrogen chloride in presence of cuprous salt; they behave, in fact, as diazo-compounds, and it is therefore essential not only to avoid the use of cupric chloride and to employ cupric sulphate, but also to purify the hydrazines.

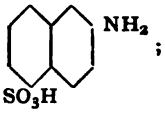
Constitution of the No. 1 Acid.—As already mentioned, this acid yields the Dahl modification of betanaphthylaminesulphonic acid on reduction. This statement is based both on the study of the properties of the reduction product, and on the further observations that it is converted by Sandmeyer's method into a chloronaphthalenesulphonic acid, yielding a monohydrated sodium salt crystallising in scales, and a chloride which crystallises from a mixture of petroleum spirit and benzene in well-defined prisms melting at 70°; and that this sulphochloride yields on distillation with PCl_5 a dichloronaphthalene which crystallises from alcohol in long, slender needles melting at 48° (*Brit. Assoc. Report*, 1888; CHEM. NEWS, lviii., 295).

The chlorosulphonic acid obtained from the No. 1 chloroamidosulphonic acid yields a monohydrated potassium salt crystallising in small, elongated plates; a chloride which crystallises from benzene in small, well-defined prisms melting at 95°; an amide crystallising from dilute alcohol in slender needles melting at 225°; and a dichloronaphthalene crystallising from alcohol in scales melting at 107°.

It was pointed out in the previous communication (*cf. Chem. Soc. Proc.*, 1889, p. 35) that γ-dichloronaphthalene must be regarded as the axially symmetric 1 : 4′ αα-heteronucleal dichloronaphthalene; the formula representing the constitution of the No. 1 acid will therefore be—



as this results on superposing the formula of the 1 : 4 chloronaphthalenesulphonic acid derived from it and that of the parent 1 : 2 chlorobetanaphthylamine. Displacing chlorine by hydrogen, the formula of the Dahl acid results, viz.,—



whence it follows that *η-dichloronaphthalene, m. p.* 48°, *is the* 1 : 3′ *dichloronaphthalene*. This result is in harmony with that arrived at by Erdmann and Kirchhoff, and serves to justify the interpretation which they have given of their synthesis of η-dichloronaphthalene.

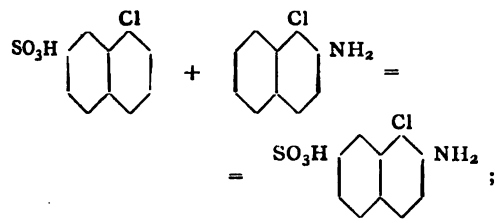
The No. 1 acid is converted by Sandmeyer's method into a dichloronaphthalenesulphonic acid which yields a potassium salt crystallising in scales; a chloride crystallising from benzene in massive prisms melting at 104°; an amide crystallising from dilute alcohol in slender, elongated plates melting at 218°; and a trichloronaphthalene crystallising from alcohol in long, slender needles melting at 78—78·5°. Dichloronaphthalene melting at 34°, which is obtained by displacing NH_2 in α-chlorobetanaphthylamine by Cl, on sulphonation yields at least two acids (*Brit. Assoc. Report*, 1888; CHEM. NEWS, lviii.,

295), from each of which the dichloronaphthalene can again be obtained by hydrolysis; one of these acids—the chief product—is undoubtedly identical with that prepared from the No. 1 chloramido-acid, as its chlorine crystallises in massive prisms melting at 105°, its amide in needles or slender scales melting at 216·5—217°, and the trichloronaphthalene prepared from it in needles melting at 78°.

Constitution of the No. 3 Acid.—On reduction this acid yields Bayer and Duisberg's betanaphthylamine-δ-sulphonic acid; the reduction product was converted by Sandmeyer's method into a chloronaphthalenesulphonic acid from which a chloride was prepared crystallising from benzene in prisms melting at 86°, and an amide crystallising from dilute alcohol in minute prisms melting at 175°; on distilling the sulphochloride with PCl_5, δ-dichloronaphthalene, m. p. 114°, was obtained (*cf. Brit. Assoc. Report*, 1888).

The chlorosulphonic acid prepared from the No. 3 acid yields a monohydrated potassium salt crystallising in small, thin scales; a chloride crystallising from a mixture of benzene and petroleum spirit in well-defined, elongated prisms melting at 93—94°; and an amide crystallising from dilute alcohol in long, slender needles melting at 185—186°; the dichloronaphthalene prepared from the sulphochloride, crystallised from alcohol in aggregates of short, slender needles melting at 63·5—64°; it was characterised by the authors' method, by sulphonation—the chloride of the resulting sulphonic acid crystallised in needles which became opaque after some time, and melted at 117—118°. This dichloronaphthalene is obtained, as the authors have shown, from Arnell's β-chloronaphthalenesulphonic acid (*Brit. Assoc. Report*, 1888; Chem. News, lviii., 295); from the Badische betanaphthylaminesulphonic acid (*ibid.; Chem. Soc. Proc.*, 1888, No. 58, p. 105); from parachlorophenylparaconic acid (Erdmann and Kirchhoff; *cf. Chem. Soc. Proc.*, 1889, No. 61, p. 7); and from Cleve's θ-α-nitronaphthalene-β-sulphonic acid (*Chem. Soc. Proc.*, 1889, No. 62, p. 18). As it is a heteronucleal α-β-derivative, it must by exclusion be the 1 : 2'-compound, as the only alternative 1 : 3' formula has been proved above to belong to η-dichloronaphthalene, m. p. 48°.

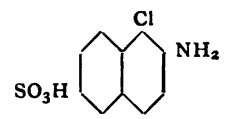
Superposing the formula which expresses the constitution of the new chlorosulphonic acid from the No. 3 acid and that of the parent chloramidonaphthalene, the formula of the No. 3 acid is shown to be as follows:—



whence it follows that Bayer and Duisberg's δ-acid is as more frequently supposed a 2 : 2'-derivative.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 3 acid yields a monohydrated sodium salt crystallising in elongated, rectangular plates; a chloride crystallising from benzene in small, well-defined prisms melting at 122—123°; and an amide crystallising from dilute alcohol in long, slender needles melting at 225—226°; the corresponding trichloronaphthalene crystallises from alcohol in hemispherical aggregates consisting of microscopic needles melting at 83—84°.

Constitution of the No. 2 Acid.—The chloronaphthalenesulphonic acid prepared from the No. 2 chloramidosulphonic acid yields an anhydrous potassium salt crystallising in small granules; a chloride crystallising from benzene in aggregates of minute diamond-shaped plates which afterwards grew into the form of opaque hemispherical aggregates melting at 112—113°; an amide crystallising from dilute alcohol in small scales melting at 185—186°; and a dichloronaphthalene melting at 48—49°: this acid is consequently identical with that described by Cleve (*Berichte*, 1887, 74), and corresponds with η-dichloronaphthalene in constitution. From this it follows that the constitution of the No. 2 acid is expressed by the formula—



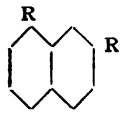
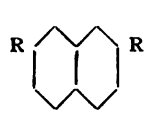
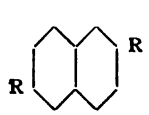
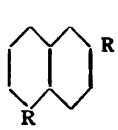
and also that it is derived from the Brönner betanaphthylaminesulphonic acid: that this is the case the authors have been able to place beyond doubt, although owing to its peculiar behaviour on reduction they have not succeeded in converting it directly into the Brönner acid.

The sodium salt of the No. 2 acid is so sparingly soluble in cold water that the reduction has to be effected at a temperature of 50—60°, and then proceeds very slowly: the liquid becomes of a dark brown colour, and yields a very dark coloured sodium salt on evaporation; this salt is soluble in 90 per cent alcohol. On acidulating a solution of the sodium salt, only a relatively very small amount of precipitate was obtained; the acid thus prepared, although evidently very impure, gave on treatment by Sandmeyer's method a chlorosulphonic acid from which a chloride crystallising in small prisms melting at 107°, and an amide crystallising in needles melting at 183° were obtained. The chloride and amide of the chlor-acid prepared by Forsling (*Berichte*, 1887, 80) from the Brönner acid have similar properties to those observed by the authors in the case of their product, and there can be little doubt therefore that the Brönner acid is formed. The chief product of reduction, however, is a very soluble acid—perhaps a hydro-derivative. If placed in contact with sodium amalgam under conditions similar to those observed in reducing the No. 2 acid, the sodium salt of the Brönner acid appears to slowly change, the solution becoming dark coloured.

When the chlorobetanaphthol corresponding to chlorobetanaphthylamine is sulphonated, it yields a sulphonic acid which is undoubtedly a derivative of Schaeffer's betanaphtholsulphonic acid—an acid which itself is convertible into and may be obtained from Brönner's betanaphthylaminesulphonic acid—inasmuch as it yields the same bromhydroxyquinonesulphonate as the Schaeffer acid on treatment with bromine, and may be converted into the Schaeffer acid by reduction with sodium amalgam. An attempt to prepare this naphthol-derivative from the No. 2 acid was unsuccessful, owing to the extreme stability of the diazo-derivative of the latter acid; on the other hand, on heating the chloronaphtholsulphonate with ammonia under pressure, a complex action took place, but a small quantity of an acid was ultimately obtained which, judging from the characteristic appearance of its sodium salt, was the No. 2 acid.

The dichloronaphthalenesulphonic acid prepared by Sandmeyer's method from the No. 2 acid gave a sodium salt crystallising in minute scales; a chloride crystallising from benzene in small aggregates of minute prisms melting at 165—166°; an amide crystallising from dilute alcohol in slender, yellow needles melting at 187—188°; and a trichloronaphthalene crystallising from alcohol in tufts of short, slender needles melting at 92°. A trichloronaphthalene of the same melting-point was obtained by submitting the chlorobetanaphtholsulphonate above-mentioned to the action of PCl_5.

The results obtained in the case of the No. 2 and No. 3 acids prove that betanaphthylamine-δ-sulphonic acid and corresponding di-derivatives of naphthalene (*e.g.*, δ-dichloronaphthalene, m. p. 114°) are 2 : 2'-compounds; and that the isomeric Brönner acid and corresponding di-derivatives (*e.g.*, ε-dichloronaphthalene, m. p. 135°) are 2 : 3'-compounds. They conclusively refute Erdmann's

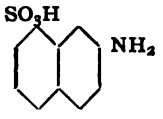
			
2 : 1′	2 : 2′	2 : 3′	2 : 4′
Cl_2. M. p. 63·5°	Cl_2. M. p. 114°	Cl_2. M. p. 135°	Cl_2. M. p. 48°
$NH_2\beta\cdot SO_3H$ (Badische)	$NH_2\beta\cdot SO_3H$ (Bayer and Duisberg)	$NH_2\beta\cdot SO_3H$ (Brönner)	$NH_2\beta\cdot SO_3H$ (Dahl)
$OH\beta\cdot SO_3H$ (Bayer)	$OH\beta\cdot SO_3H$ (Casella)	$OH\beta\cdot SO_3H$ (Schaeffer)	$OH\beta\cdot SO_3H$ (Dahl)
$NO_2\alpha\cdot SO_2Cl$ M. p. 169°	—	—	$NO_2\alpha\cdot SO_2Cl$ M. p. 125°
—	$(SO_3H)_2$ (Ebert and Merz α)	$(SO_3H)_2$ (Ebert and Merz β)	$(SO_3H)_2$ (Armstrong and Wynne)
$Cl\alpha\cdot SO_2Cl$ M. p. 94°	—	—	$Cl\alpha\cdot SO_2Cl$ M. p. 114°
$Cl\beta\cdot SO_2Cl$ M. p. 129°.	$Cl\beta\cdot SO_2Cl$ M. p. 86°	$Cl\beta\cdot SO_2Cl$ M. p. 109°	$Cl\beta\cdot SO_2Cl$ M. p. 70°.

statement (*Berichte*, 1888, 639): "Diese Frage (as to whether the Brönner and δ acids are respectively 2 : 3′ and 2 : 2′ compounds, or *vice versâ*) ist nur durch synthetischen Aufbau dieser oder ähnlichen Verbindungen zu lösen"—indeed notwithstanding it has been their privilege to confirm Erdmann and Kirchhoff's conclusions, the authors remain of the opinion that a synthetic method, such as these chemists have so successfully employed, does not and cannot afford a final solution of the problem, although their results undoubtedly serve to increase our belief in the general trustworthiness in such cases of conclusions based on the application of synthetic methods.

The results also establish the correctness of the opinion, long held and frequently expressed by the authors, based on the higher melting-points of the uniform ε-di-derivatives in comparison with the isomeric δ-di-derivatives, that the ε-derivatives are symmetrically constituted; this conclusion, in fact, is probably the most important outcome of the experiments, as it affords conclusive proof of the influence of symmetry as the determining cause in the case of naphthalene-derivatives of high melting-point and slight solubility, &c.

It has already been pointed out that the dichloronaphthalenesulphonic acid prepared from the No. 1 acid is identical with the chief product of sulphonation of 1 : 2 dichloronaphthalene; the dichloro-acid prepared from the No. 2 acid is found in like manner to be identical with the second acid formed on sulphonating the dichloronaphthalene in question. As the one acid is an alpha-sulphonic acid and the second a beta-sulphonic acid formed by displacement of the hydrogen-atom contiguous to that which is displaced in the α-sulphonic acid, the authors are of opinion that the beta-sulphonic acid is a product of isomeric change and not a product of initial action; they propose to investigate this question in the manner already adopted with success in the case of the acids derived from β-chloro-, β-bromo-, and β-iodonaphthalene.

Lastly, it may be pointed out that as the Badische betanaphthylaminesulphonic acid is now proved to have the constitution represented by the formula—



the remarkable fact that this acid alone of the our known heteronucleal betanaphthylaminesulphonic acids does not afford azo-colours must be regarded as a result of a "protecting influence" of the amido and sulphonic radicles on the included α-hydrogen atom, and the non-occurrence of the isomeric change which would be involved in the conversion of the diazoamido-compound initially produced by the action of the diazo-compound into the quinonoid azo-colour (*cf. Chem. Soc. Proceedings*, 1888, No. 49, p. 29); it is noteworthy that the isomeric change does take place in the case of the corresponding hydroxy-acid (Bayer's croceinic acid) although the colour is formed but slowly, and it is not improbable that it may be found possible by varying the diazo-compound to obtain colours even from the Badische amido-acid. The authors propose to undertake experiments in this direction.

The constitution of a number of heteronucleal di-derivatives of naphthalene which are of importance as reference compounds is indicated in the table above, the compounds being represented by the symbols of the constituent radicles. The authors take this opportunity of directing the attention especially of Continental colleagues to the desirability of adopting a uniform system of notation; they would advocate that which has long been in use by the Chemical Society, which consists in numbering the positions in the one nucleus 1, 2, 3, 4, and the corresponding positions in the second nucleus 1′, 2′, 3′, 4′. This method they regard as more rational, in view of the fact that naphthalene contains two like nuclei, than the practice now sometimes adopted of numbering the positions 1 to 8.

32. "*Contributions to the Knowledge of Citric and Aconitic Acids.*" By S. Skinner, B.A., and S. Ruhemann, Ph. D., M.A.

The authors have studied the action of phosphorus pentachloride on citric acid, following Pebal's directions (*Annalen*, xcviii., 67). They show that the product is a chloromonochloride formed by the displacement of the alcoholic hydroxyl and one of the carboxylic hydroxyls, it being uncertain, however, which of the three latter in citric acid is affected. The chloride is reconverted into citric acid by the action of water; when heated at 125°, it loses hydrogen chloride, yielding a product which water converts into aconitic acid; aniline transforms it into aconitylanilanilide, and it is similarly affected by treatment with orthotoluidine. The anilanilide yields the anilcarboxylic acid and aniline on hydrolysis, and the toluidine-derivative affords the corresponding toluidcarboxylic acid.

NOTICES OF BOOKS.

A Treatise on Manures, or the Philosophy of Manuring: A Practical Handbook for the Agriculturist, Manufacturer, and Student. By A. B. Griffiths, Ph.D., F.R.S. (Edin.), F.C.S., Principal and Lecturer on Chemistry, the School of Science, Lincoln. London: Whittaker and Co. and G. Bell and Sons.

This manual forms one of the valuable "Specialists' Series," now in course of publication by the two firms above mentioned. The author takes as his motto the saying that:—"There is not a farmer in England, however primitive and however unconscious of the fact, but is now conducting his business more or less on lines emanating from the laboratory." Yet at the same time we find that the failures of the farmer are due to ignorance of the exact nature and requirements of the soils and of the crops he may desire to grow, or to prejudice against the use of artificial manures.

Elsewhere we read:—"The farmer in this country must keep pace with the times if he is to compete with foreign nations who fully recognise the great value of science as applied to agriculture."

Perhaps, however, the most fatal prejudice of the British people is that which leads it, both at home and in the colonies, to devote itself, alike in agriculture and in manufactures, to the production of a few gigantic "staples," neglecting minor industries which, if individually trifling, sum up in their results to an enormous total.

Passing over this consideration as concerning the economist rather than the chemist, we come to the author's elaborate examination of the use of ferrous sulphate as a manure. In the seasons 1883, 1884, and 1886 Dr. Griffiths grew bean crops with and without the application of this salt. On each of two plots, agreeing very closely in the composition of the soil and identical, as we gather, in exposure, texture, and drainage, was planted on the same day an equal number of bean-seeds. The crop grown with the addition of ferrous sulphate at the rate of ½ cwt. per acre yielded 56 bushels of dry beans, whilst the corresponding plots without the copperas produced only 35 bushels. Corresponding experiments in other seasons gave similarly favourable results. With various other crops, *e.g.*, turnips, hay, mangel wurzel, potatoes, wheat, cabbages, and onions, dressings of ferrous sulphate have given advantageous results. The copperas, it will be noticed, is to be superadded to the other manurial agents and not used as a substitute. It is also recommended as an antidote for various microscopic fungi, and it is stated on the authority of MM. Berthelot, Gautier, and Drouin that iron oxides accelerate the process of fixing atmospheric nitrogen in a soil. That iron in certain quantities, *i.e.*, in the neighbourhood of Wellington College, act as plant poisons and sterilise the soils is fully admitted. But the proportion found producing such effects is more than eighty times greater than the dose recommended by the author. The unfavourable results said to have been obtained with the dissolved basic slag, patented by Messrs. Wrightson and Munro, seem to be referrible to the excessive dose, as nearly 1¼ cwt. of ferrous sulphate must have been applied to the acre.

Basic slag (Thomas and Gilchrist) finely ground is recommended as a phosphatic manure. The author estimates that the 100,000 tons of this residue annually produced in England would suffice to raise four million tons of hay, and thus feed three quarter million head of cattle. The manure from these cattle would subserve the production of more thon a million tons of grain. "This amount of grain and cattle is more than twice the quantity of these foods we haye ever imported, and, according to the smallest calculation, the yearly saving to this country would be 11½ millions sterling. One condition is, however, of importance as regards the grain, that we should not have such summers as those of 1879 and 1888.

M. Ville's system of manuring is pronounced "worthy of the deepest study on the part of British farmers and others." It is remarked that this author, in addition to his four essential constituents of artificial manures, has been led to recognise the value of soluble iron-compounds. Gypsum Dr. Griffiths considers better adapted to the soils—or the climates—of the Continent rather than those of Britain.

As regards the valuation of manures, the author shows that a manure has two distinct values; a *commercial* value, turning solely on supply and demand, and an *agricultural*, which depends on the requirements of the crop to which it is to be applied, and to the deficiencies or redundances of the soils in which they are to be planted. If a manure is to be profitable to the farmer its agricultural value must exceed its commercial value. In other words, it must fetch less money out of his pocket than the value of the produce which it fetches out of the soil.

Other features of this work, which space does not allow us to notice, are the account of the various ingredients used in manures, of the manufacture of superphosphate and other artificial fertilisers, and the directions for the analysis of manures.

The work is indeed a *multum in parvo* of information valuable to the manure-maker and the practical farmer, and must be most strongly recommended.

Nature Series: The Chemistry of Photography. By Raphael Meldola, F.R.S. London: Macmillan and Co.

In the preface to this volume we find quoted an apparently paradoxical but really most significant saying of the late Colonel Russell's, that "Photography would be a most interesting subject *were it not for the pictures*." It is somewhat curious that in an age when we are literally beset with photographers, amateur and professional, the principles underlying the mere routine practice of the art should be so generally ignored. To meet this widespread shortcoming Prof. Meldola has delivered at the Finsbury Technical College the course of special lectures which form the subject-matter of the work before us. How fully the author comprehends the necessities of the situation will be at once gathered from the following passage, which, we must take leave to add, might, *mutato nomine*, be applied to not a few other arts:—"I am disposed to believe that the art is in danger of outstripping the Science. This is a state of affairs which we often witness when a discovery of immediate practical utility is made. There are many branches of industry which are now suffering in this country because they have been allowed to go on from the time of their foundation without any attention being paid to the scientific principles underlying them. It has been found by a long course of experience that certain results can be obtained in a particular way, and that mode of procedure has become stereotyped into a kind of article of faith. In such cases no trouble is taken to ascertain *why* the particular mode of operation leads to the desired results—the art has here outstripped the science. But if we thus allow a useful discovery to degenerate into a purely empirical industry we are neglecting our duty to that science which first gave us the discovery; and not only this, but we are running into the danger of seeing the industry taken out of our hands by more scientific competitors, who have no stereotyped formulæ, and who have taken the trouble to investigate the why and the wherefore of the different steps of their processes."

Prof. Meldola, accordingly, does not, in the work before us, attempt to deal with photography as an *art*. He does not even propose to enter upon the chemistry of the *materia photographica*. He is concerned with the chemistry of photographic processes and the principles

involved, so that the reader may see what remains to be learnt and in what direction improvement seems necessary and practicable. There are, as the author points, many chemical actions effected by light which cannot be directly brought in connection with the photographic process. These would have proved interesting and apposite subjects in a general work on photo-chemistry, but they lie beyond the scope of the present treatise.

Among the first questions discussed is the action of light on silver chloride. The change which takes place is ascribed in the text-books to the formation of a subchloride, consequent upon the loss of chlorine. But Prof. Meldola, though he admits that the violet chloride contains less chlorine than the unaltered white chloride, shows good reason for questioning the formation of Ag_2Cl, and considering that the compound in question has never yet been isolated, and consequently has not been analysed, he considers that the safest course is to view the violet compound as a reduction-product of unknown formula.

The production of photographic pictures in their natural colours is admitted to be a problem which has never been solved. The author mentions the experiments in this direction of Seebeck, of Sir J. Herschel, Becquerel, Niepce de St. Victor, Poiteven, Carey Lea, and G. Staats. In these experiments variously coloured impressions have been produced. But their fixation has so far not been found practicable. Research in this direction is, however, mentioned as being of interest.

After each chapter we find an appendix describing experiments proving or illustrating the points advanced.

The "Chemistry of Photography" is, in our judgment, a timely production executed by a most competent authority.

Introduction to the Study of the Chemistry of the Ancients and of the Middle Ages ("Introduction à l'Etude de la Chimie des Anciens et du Moyen Age"). By M. Berthelot, Professor in the College of France. Paris: Georges Steinheil.

Men of science, and especially chemists, are generally more concerned with the future than with the present, and still more than with the past. Yet none of us, surely, can read M. Berthelot's work on the infancy of our science without profound interest and without feeling deeply indebted to the writer, who has devoted six years of a busy life to sweeping away certain widespread and deeply rooted errors.

It is commonly said and believed that chemistry had its origin in "alchemy," that word being taken to signify a tissue of mystical dreams on the transmutation of metals and on the elixir of life, diversified with occasional attemps to carry these beliefs into practice. This mistake—for that it is a mistake every reader of the work before us will become convinced—has not been without serious consequences. It has been a main pillar of the heresy that every science must pass successively through three stages—a mystical or mythological, a metaphysical, and finally a "positive." Such, it will be seen, was not the case: chemistry took its rise in the workshops of old Egyptian metallurgists, goldsmiths, and dyers—crafts which were in those days, strangely enough, practised by the same artizans. We find here a curious collection of recipes translated from the "Papyrus X" of the Leyden collection, which, from evidence internal as well as external, dates back to the third century of our era. These recipes show a knowledge of chemistry, certainly limited, but totally free from anything visionary or mythological. Here and there occurs a word which cannot be translated, but in the language and in the purport of these receipts there is no more mysticism than may be found in any modern cyclopædia of chemical recipes. As far as they go they are perfectly matter-of-fact and "positive." We find directions for purifying tin, for hardening lead, for colouring gold, for increasing the weight of gold, for whitening copper, for making a solder for gold, for writing in letters of gold, for giving copper the appearance of gold, for making base metal bear the trial by the touchstone, &c. Not a few of these prescriptions are for objects which cannot be called other than fraudulent. And here we find the transition to alchemy in the ordinary sense of the term. The ancient, adept from deceiving others, was gradually led to deceive himself. Finding that he could apparently multiply gold and silver, the thought dawned upon him that he might do so in reality. He hoped that as a small quantity of yeast vivifies a large volume of saccharine fluid, so a little gold might set up a fermentation in base metal, by which the whole should be ennobled. From this point dates the introduction into chemistry of that mystical element.

M. Berthelot has devoted much patient research to interpreting the peculiar terms and symbols of the old alchemists. All who feel an interest in this portion of the history of our science will find in this volume and in the two preceding works, the "Origines de l'Alchimie" and the "Collection des Alchimists Grecs," a safe guide. We learn that several discoveries supposed to have been made in comparatively modern days may be traced back to a remote antiquity. Thus, cobalt is commonly said to have been first obtained by Brandes in 1742, and its name is connected with certain malignant demons which interfered with the work of the miner. In fact, cobalt was known to the ancients in the days of Theophrastus (though it had not been isolated), and was spoken of as the "male blue," in opposition to the "female blue" derived from the compounds of copper. The very name cobalt is traced to the Greek. Thus in the "Lexicon Alchemiæ Rulandi," we read:—"*Cobatiorum* fumus est kobalt." The expression "fume of cobathia" is to be found in a passage of Hermes, cited by Olympiodorus. Even metallic cobalt seems to have been known as early as 1612. Metallic antimony was also known in ancient Chaldea long before its reputed discovery by Basil Valentine, a semi-mythological personage. The very name "antimony" is derived, not from its legendary poisonous action upon monks, but from the Arabic "athmoud" or "othmoud."

It appears that the autogenous soldering of lead, commonly supposed to be a modern discovery, is described by Vincent de Beauvais in his "*Speculum majus*" as being actually in use. Wood was rendered incombustible, according to Aulus Gellius, by steeping in or coating with alum. The fire-proof textiles of the ancients were woven from asbestos. In fact, in our knowledge of the useful arts, we have not made, in comparison with the days of classical antiquity, such gigantic strides as it is commonly supposed. Had the technical writings of the Egyptians not been destroyed by the Emperor Diocletian and by the ignorant zeal of the early Christians we should doubtless meet with astonishing revelations.

CORRESPONDENCE.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—Mr. J. G. McIntosh (Chemical News, vol. lix., p. 167) confounds the old experiments with iron sulphate with those of later date.

The old experimentalists used *large* quantities of iron sulphate as a manure, and, in many cases, failed in producing anything like a satisfactory yield; whereas in the experiments recorded in the *Journal of the Chemical Society* during the past few years, only ¼ cwt. of $FeSO_4$ per acre were used, with the greatest benefit, for certain crops, proving that it is a *direct* as well as indirect plant food.

Concerning Mr. McIntosh's remarks about the late Dr. Voelcker's experiments, I may say that even Voelcker

was preceded by Prince Salm-Horstmar (*Annales de Physique et de Chimie*, 1851).

Mr. McIntosh says:—"It is strange that sulphate of *ammonia* has not gone down to 10s. per ton if we are to credit what "X" says in regard to what Professor Muntz says." I think he must have made a slip of the pen. Ammonium sulphate is a valuable *nitrogenous* manure, and was not included among the sulphates. Even Mr. McIntosh *did not* include it among the sulphates he mentioned in the CHEMICAL NEWS (vol. lix., p. 96).

There are many fresh details recorded in the recent memoirs published in the *Journal of the Chemical Society* (1882—87), or why did the Council of the Society think fit to give them a place in the *Transactions*?

What about (*a*) the displacement of K_2O in the ashes of those plants grown with $FeSO_4$ and, also, an increase of P_2O_5 and Fe_2O_3. (*b*) The increase of chlorophyll, albumenoids, and soluble carbohydrates in those crops grown with $FeSO_4$. (*c*) The increased yield and improved quality of crops grown by its aid?

These details have been confirmed by Muntz, Porion (the *confrère* of Dehérain), Delacharlonny, and others (*La Sucrerie Indigène et Coloniale*, vol. xxxi., p. 571).

Again, what about the germicidal properties of $FeSO_4$, its power for destroying *Peronospora infestans*, *wheat mildew*, *moss* in mossy pastures, &c.? These experiments have also been confirmed in France (*Journal de l'Agriculture*, Sept., 1887, and *Bulletin de la Société d'Horticulture de Soissons*, 1887).

I think it would be well for your correspondent to perform a few experiments on the subject before he criticises the work of others.—I am, &c.,

"X"

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 13, April 1, 1889.

A Periodic Balance of Precision Admitting of the Direct Reading of the Ultimate Weight.—P. Curie.—This balance cannot be described without the accompanying figure.

The Law of the Solubility of Gases.—M. Woukoloff.—If carbon dioxide does not rigorously follow Dalton's law when it dissolves in carbon disulphide the deviations are very small, and of the same rank as those which it shows as regards the law of Mariotte. At low temperatures its absorption is greater and at high temperatures higher than the law demands.

On Succinamic Nitrile.—René Drouin.—This compound appears in the form of small colourless clinorhombic crystals, scarcely soluble in alcohol, even when hot, insoluble in ethyl ether, chloroform, essence of turpentine, benzene, petroleum, and carbon disulphide, decomposed slowly by cold water and more rapidly by hot water, with escape of ammonia.

Researches on the Alkaloids, Artificial and Natural.—Albert Colson.—The author describes the chlorostannite, the hydrochlorate, and the hexabromo-derivative of a base, $C_{22}H_{18}N_2O_3$, and certain bromine derivatives of quinine.

Analysis of the Sewage of Paris.—M. Aymonnet.—The sewage in question was drawn at the outfall of the Clichy sewer. The author has merely determined the nitrogen transformed into ammonia by magnesia and boiling water (method of Boussingault and Schlœsing) and the total nitrogen less nitrates obtained by the Frankland and Armstrong process.

Zeitschrift fur Analytische Chemie. Vol. xxviii., Part 1.

Separation of Alumina from Ferric Oxide.—Chancel.—From the *Comptes Rendus*.

Determination of Titanium in Iron and Iron Ores.—A. Ledebür (*Chemiker Zeitung*).

Qualitative Separation of Tin and Mercury.—Th. Wilm (*Journal Russ. Phys. Chem. Gesellsch*).—If a mixture of mercury chloride and tin tetrachloride is mixed with yellow ammonium sulphide the mercury remains chiefly in solution along with the tin, as a double compound of the two sulphides soluble in the ammonium polysulphides.

A Rapid Volumetric Method for the Determination of Boric Acid.—Hans Will.

Distinction between Tannin and Gallic Acid.—J. E. Saul.—From the *Pharmaceutical Journal*.

Detection of Acetanilide.—A number of methods are given by Vulpius, Yvon, Della Cella, Arzen, and Flückiger.

Execution of the Dumas Nitrogen Process.—W. Hankó.—The author proposes a modified apparatus, which is here figured.

Determination of Tannin in Tan and Dye-wares.—The principal processes here described are those of H. R. Procter (*Journal of the Society of Chemical Industry*). Villon, noticed under *Bulletin de la Soc. Chimique de Paris*, and Collid and Benoist (CHEMICAL NEWS).

Detection of Saccharine in Beer.—A. H. Allen.—From the *Analyst*.

Detection of Fusel in Spirits.—E. Sell (*Kaeseil. Gesundheit's Amt.*).—The author's process is not described.

On Cacao Starch.—P. Saltsien (*Archiv der Pharmacie*).—The author shows that, contrary to the common opinion, cacao starch, when pure, gives the ordinary blue colour with iodine.

Adulteration of Tinned Tomatoes.—M. Carles.—From the *Journal de Pharmacie*.

Stability of Explosives on Exposure to Heat.—O. Hagen (*Repert. Anal. Chem.*).—No particulars are given.

Examination of Oil of Almonds.—G. Vulpius (*Archiv der Pharmacie*).—No particulars are given.

Further Test for Aloes.—Messrs. Cripps and Dymond.—From the *Pharmaceutical Journal*.

Reactions of Colours on the Fibre.—R. Lepetit.

MISCELLANEOUS.

University of London.—We are requested to draw the attention of Candidates for Matriculation to the fact that the June Examination is, in the present and future years, to be held a week earlier than heretofore.

Detection of Resin (Colophonium).—Th. Morawski (*Chemiker Zeitung*).—The author founds a process on L. Storch's reaction for detecting resin-oil by means of acetic anhydride and sulphuric acid. A particle of the substance is dissolved in acetic anhydride at a gentle heat, the solution is cooled, and a drop of sulphuric acid (undiluted) is cautiously let flow down the side of the test-glass. In presence of resin, or resin-oil, there appears an intense red to violet-blue colour, which soon disappears, leaving the liquid brownish yellow and fluorescent.

MEETINGS FOR THE WEEK

TUESDAY, 23rd.—Royal Medical and Chirurgical, 8.30.
THURSDAY, 25th.—Institute of Electrical Engineers, 8.
FRIDAY, 26th.—Quekett Club, 8.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1535.

ON THE

CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

By RACHEL LLOYD.

(Continued from p. 188).

Thymol.

The object of the following research was the study of the action of zinc-ammonium bromide upon some of the phenols of a more complicated chemical structure. To this end thymol was selected as the starting-point.

The thymol used distilled at 230°.

The same proportions by weight of phenol, zinc-ammonium bromide, and ammonium bromide, 1 : 3 : 1, were used as in former experiments, the mixture was heated for forty hours, and the temperature raised to 350°—360°. The tube-contents presented distinctly marked layers. The upper layer, an amorphous mass of a dark brown colour, was intermingled with many lighter particles of an indistinct crystalline form. The under layer, a lighter coloured amorphous mass, was impregnated with a dark oily liquid. Water was formed in abundance. Pressure in tubes, very slight. The contents of the tubes were warmed with dilute hydrochloric acid, then with ether under return-condenser, and the bases separated according to previously described methods.

Thymylamine :—

$$N\begin{cases}C_{10}H_{13}\\H\\H\end{cases} = C_{10}H_{13}NH_2$$

separated as a very light coloured oil, which, after two distillations, boiled constantly at 230°.

With sulphuric acid and potassium bichromate it gave the characteristic reaction ; in the degree of its solubility in the ordinary solvents and in its compounds it showed its identity with the cymylamine obtained by Widman† from cuminol.

Dithymylamine :—

$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\H\end{cases} = C_{20}H_{26}NH.$$

The impure secondary amine, a dark smeary mass of indistinct crystalline structure, was purified by repeated distillation with super-heated steam and fractionation in an atmosphere of hydrogen. The greater portion of the oil distilled between 340°—345° ; while above 346° partial decomposition took place with evolution of yellow fumes.

The so-obtained almost colourless base, which was not solidified at −18° C., had a pleasant aromatic odour, gave with sulphuric acid a golden-brown colour with a tinge of red : slight fluorescence was noticeable. Nitric acid added to this solution changed the colour at once to dark blue, which remained unchanged. With a nitrite, a greenish blue tint was produced.

The presence of a secondary amine was confirmed by the analysis ;—

I. 0·1355 grm. substance gave 0·4264 grm. carbon dioxide and 0·1138 grm. water, corresponding to 0·1163 grm. C. and 0·01264 grm. H.

II. 0·1255 grm. substance gave 6 c.c. moist nitrogen (thermometer 22° C., barometer 727 m.m.), equal to 0·006494 grm. N.

Calculated for $C_{20}H_{27}N$.		Found.
C_{20} − 240 −	85·41 per cent	.. 85·82 per cent
H_{27} − 27 −	9·61 „	.. 9·33 „
N − 14 −	4·98 „	.. 5·17 „
281 −	100·00 per cent	

Accompanying these bases was unchanged thymol, which was isolated and weighed. Corresponding experiments were made with thymol and the chloride of zinc and ammonium. The results of repeated experiment are here given. The proportion of the substances used, as well as the time and temperature, were the same as when the bromides were used.

	Zinc-ammonium bromide.			Zinc-ammonium chloride.		
Thymol.	I.	II.	III.	I.	II.	III.
Thymylamine	25	21·5	29	23	24	22·6 p.c.
Dithymylamine ..	24	30	28·5	20	25	20·5 „
Unchanged thymol..	45	40	39	48	26	44·3 „
Carbonised substance	1	0·5	0·9	2	1·9	2·3 „

Derivatives of Thymylamine.

The platinum double salt—$(C_{10}H_{15}N.HCl)_2PtCl_4$—was prepared by dissolving the base in absolute alcohol, adding a small amount of hydrochloric acid, then an alcoholic solution of platinum chloride in excess. The double salt separated at once in the form of golden needles. These were re-crystallised from absolute alcohol. The crystals warmed with water were decomposed with separation of the base.

An analysis of the salt dried at 100°—110° gave the following result :—

I. 0·1736 grm. substance gave 0·0476 grm. platinum.

II. 0·6944 grm. substance gave 0·19040 grm. platinum.

Calculated for $(C_{10}H_{15}N.HCl)_2PtCl_4$.	Found. I.	II.
27·48 per cent Pt. ..	27·41 ..	27·42 per cent Pt.

Acetylthymylamine :—

$$N\begin{cases}C_{10}H_{13}O\\C_2H_3O\\H\end{cases} = C_{12}H_{17}NO.$$

The compound was formed by heating the base with an excess of acetic anhydride for half an hour at 100°. The solution, which at first was almost colourless, changed to a light brown ; upon cooling, a greyish white crystalline mass separated, which was washed and neutralised with sodium carbonate and re-crystallised from absolute alcohol, in satiny white needles which melted at 112·5°, closely agreeing with the melting-point obtained by Widman.*

Derivatives of Dithymylamine.

The *platinum double salt*—$(C_{20}H_{26}NH.HCl)_2PtCl_4$—was formed when, to an ether solution of the base acidified with hydrochloric acid, platinum chloride was added in excess. After standing for some days, a thick yellowish brown oil separated, which was thoroughly washed in cold alcohol (in which it was not soluble), dried over paraffin and sulphuric acid, and finally at 100°.

The analysis gave the following result :—

0·1630 grm. substance gave 0·03241 grm. platinum.

Calculated for $(C_{20}H_{26}NH.HCl)_2PtCl_4$.	Found.
20·01 per cent Pt.	19·88 per cent Pt.

Acetyldithymylamine :—

$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\C_2H_2O\end{cases} = C_{22}C_{29}NO.$$

* "University Studies, Published by the University of Nebraska," October, 1888.

† *Berichte der Deutschen chem. Gesellschaft*, xv., 166.

* *Berichte der Deutschen chem. Gesellschaft*, xv., 166.

This body was formed by heating together calculated amounts of the base and acetic anhydride at a temperature of 130°—135°. At the end of an hour the reaction was complete. The product, a yellowish white mass, was crystallised from benzol in white leaflets which melted at 78°, dissolved readily in hot benzol and ligroin, sparingly in alcohol.

An analysis gave the following result:—

0·1929 grm. substance gave 0·5760 grm. carbon dioxide and 0·1589 grm. water, corresponding to 0·15708 grm. C. and 0·1765 grm. H.

Calculated for $C_{22}H_{29}NO$.			Found.
C_{22}	— 264 —	81·73 per cent . ..	81·43 per cent
H_{29}	— 29 —	8·98 „ . ..	9·15 „
N	— 14 —	4·34 „ . ..	— „
O	— 16 —	4·95 „ . ..	— „
	323 —	100·00 per cent	

(To be continued).

ON THE ANALYSIS OF CINCHONAS, AND ON THE RELATIVE SOLUBILITY OF THEIR PROXIMATE PRINCIPLES IN WATER, ALCOHOL, AND DILUTE HYDROCHLORIC ACID.

By ED. LANDRIN.

The type of bark selected for the experiments was the *Cinchona succirubra*, derived from the plantations of the Dutch Government in Java. The author takes 300 grms. of the bark to be assayed and reduces it into powder sufficiently fine to pass through a No. 40 sieve. He prepares a milk of lime with 75 grms. caustic lime, adding 75 grms. of a solution of caustic soda at 40° B. and 1 litre of water. The bark is poured into this mixture so as to be homogeneous, and if it is too thick it may be diluted with a little water. The mixture of lime and soda is very important for liberating the total alkaloids of the cinchona. Since he has used this method his results do not vary by more than 1 part in 1000. He then pours upon the mixture 2 litres of oil of shale, which is raised to the temperature of 100° for twenty minutes, stirring the cinchona and the oil constantly so that all parts may come constantly in contact. The oil saturated with alkaloids is then decanted off, two more litres of oil are then added, and the operation is repeated exactly as before. We have then all the alkaloids of the bark in solution in the four litres of oil. The first treatment carries off, on an average, nine-tenths of the alkaloids. A third treatment with oil would be useless. The four litres of hot oil are then washed, at first with 75 c.c. of water acidulated with sulphuric acid at one-tenth, to which 150 c.c. of water have been added. This washing is continued for ten minutes, and then the acid liquid is poured off. The operation is repeated a second time with the same quantities of the same liquid, and a third time with a quantity one-half less. The two first acid liquids are poured together and neutralised with ammonia at a boiling heat in order to separate resinous matter. The same is done with the third acid liquid, which serves to wash the filter of the first operation. On cooling, the proportion of acid liquid with respect to the cinchona employed is such that the larger proportion of the alkaloid salts, on the mean nine-tenths, crystallise out. These sulphates are separated by filtration and the mother-liquors are precipitated with caustic soda. The alkaloids, drained, dried, and pressed, are taken up in a minimum of acidulated water, so as to transform them into sulphates without acidifying the liquid. The total sulphates are weighed and their separation is effected by known methods. It appeared that the sample of bark examined contained per kilo.—

Total alkaloids	.. .. ..	75·92 grms.
Crystalline salts	.. ..	51·83 „
Quinine sulphate	.. ..	21·27 „

The author finds that water extracts from cinchona bark the chief part of its active principles. Alcohol at 90° extracts from bark approximately the same quantity of alkaloids as water, but dilute hydrochloric acid, contrary to the general opinion, extracts less.—*Comptes Rendus* (vol. cviii., p. 750).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, April 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, two were recorded as "very slightly turbid." The remaining 180 samples were clean, bright, and well filtered.

During the month of March, the water furnished to the Metropolis by the seven Companies taking their supply from the Thames and the Lea, has continued to exhibit the wholly satisfactory character commented on in our last month's Report. The mean results afforded by the three different methods of examination employed, namely, the daily estimation of the degree of colour-tint of each Company's water, the daily estimation of the amount of oxygen absorbable from permanganate by each Company's water, and the weekly estimation of the proportion of organic carbon present in each Company's water—the three methods of examination acting as checks upon one another—are, in the case of all three methods respectively, as nearly as possible identical with the mean results afforded by the examination of the previous month's supply.

During the first three months of the year we have examined a total of 537 samples of the water supplied to the Metropolis by the above-mentioned Companies. Seven of these samples were recorded as exhibiting, under careful examination, a "very slight" degree of turbidity or deficiency in absolute clearness. The maximum proportion of organic carbon present in any single sample of water examined (early in January) was 0·197 part—the mean proportion in the Thames derived supply for the

three months being 0·164 part—in 100,000 parts of the water. Since January, the maximum proportion of organic carbon present has not exceeded 0·175 part in 100,000 parts of the water. It is to be noted, moreover, that the above are the results afforded by examinations of the water supply conducted during an eminently unfavourable season of the year.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

THE CORROSION AND FOULING OF STEEL AND IRON SHIPS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

The difficulty of obtaining adequate experimental data, and the fact that nearly everyone who has worked at the subject has had a composition of his own to bring before the public, has so hampered and restrained the free discussion and interchange of ideas on this most important question, that at the present time we have made but scant progress beyond the point reached twenty years ago, and my object in bringing this paper before you is more to excite you to discussion, and to show you the known facts of the case, than to tell you of any very new or startling discoveries.

Corrosion generally precedes fouling on exposed metal surfaces, and it is therefore this portion of the subject that will be considered first, together with the means which have been taken to prevent it, and to protect the plates of our vessels from decay.

In a paper which I had the honour to bring before you two years ago, I pointed out that in all processes of rusting, carbonic acid gas and moisture played an important part, the iron uniting with the carbonic acid and oxygen of the water to form ferrous carbonate whilst the hydrogen was set free, and that the ferrous carbonate then took up oxygen dissolved in the water or present in the atmosphere, as the case may be, and was decomposed into ferric oxide (rust) and carbonic acid, which being liberated in actual contact with the moist surface of the iron, carried on the process of "rusting."

This view of the case was confirmed by a paper read by Professor Crum Brown before the Iron and Steel Institute, at Edinburgh, last autumn, and is generally accepted as the true explanation of the corrosion taking place on iron or steel surfaces exposed to moist air or fresh water; but the rusting of the metal in sea-water has by many chemists been ascribed to a more complex action, in which the salt present plays an important part by first forming oxychloride of iron.

This preliminary stage of corrosion in sea-water is, I am inclined to think, a myth. When iron filings or turnings are exposed to the action of sea-water, hydrogen gas is evolved, and ferrous oxide and carbonate are formed; and this changes, as in air or fresh water, into ferric oxide by taking up dissolved oxygen present in the water. At no time have I been able to detect the presence of oxychloride, and from the fact that a few drops of alkali added to the sea-water stop the corrosion, I am of opinion that the simple rusting of iron in sea-water is due to the same cause as in fresh—*i.e.*, the decomposition of the water by the iron in presence of carbonic acid.

The saline constituents of sea-water, however, do undoubtedly play an important part in a more active form of corrosion, by helping to excite galvanic action between the iron in the plates and any foreign metal or impurities present, an action which is also materially aided by want of homogeneity in the metal, by particles of rust, by mill scale, by wrought and cast-iron or steel in contact with each other; or even by the different amount of work, such as hammering or bending, undergone by different parts of the same plate; and in all of these cases the galvanic action set up causes rapid oxidation of the iron at the expense of the oxygen of the water, hydrogen being evolved.

We may therefore consider that on the skin of a ship two processes of rusting are going on, the one simple corrosion on exposed surfaces of the metal, due to the presence of moisture, carbonic acid, and free oxygen, which forms a fairly uniform coating of rust on the metal, and the more local corrosion due to galvanic action, which results in pitting and uneven eating away of the plates.

As I pointed out in my previous paper, rust cones are due to the most local form of galvanic action, caused by the presence of a spec of deposited copper, lead, or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and antifoulers; as soon as the sea-water penetrates to these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister, the hydrogen leaks out, and water leaks in, the action becoming becoming more and more rapid, and the blister gradually filling with the result of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being perfectly visible in a well-formed cone; and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

The spec of foreign matter which has caused this destructive action generally clings to the surface of the iron, and being at the bottom of the pitting escapes detection and removal; and when the vessel, newly coated with fresh compositions, again goes to sea, the corrosion will again probably be set up in the same spot.

The corrosion of the plates in the interior of a vessel is a subject quite equal in importance to the external action of sea-water and dissolved gases on the metal; and from the fact that certain portions of the interior plates from their position escape the frequent examination and attention bestowed upon the exterior, it becomes a still greater source of danger.

Corrosion, like all other forms of chemical action, is much accelerated by increase of temperature; and in the bottom of a ship near the furnace-room and boilers, this has a considerable effect in increasing the rapidity of rusting. Also in the coal-bunkers, the mere contact of moist coal with the iron plates sets up galvanic action, carbon being electro-negative to iron, and the coal dust which sifts down into the double bottoms lends its aid to the destruction of the plates; whilst if the coal contains any "pyrites," which is nearly always the case, these doubles sulphides of iron and copper are gradually oxidised into soluble sulphates of the metals, and these, washing down into the bilge water, would at once cause most serious corrosion, should they come in contact with any bare portion of the plates. Repairs to any portion of the inside plates will loosen rust and mill scale, which, finding its way into the bottom, tends to set up galvanic action; whilst the scale of oxide of copper from copper and brass fittings and pipes is another great cause of danger, as the bilge water would gradually convert it into soluble salts, which will deposit their copper upon the iron wherever a crack or abrasion enables them to come in contact with it; and finally, leakages from stores and cargo are in many cases of a character highly injurious to iron.

In addition to all these sources of danger, we must remember that the interior of the vessel is the part most

* Read at the Thirtieth Session of the Institution of Naval Architects, April 12th, 1889. The Right Hon. the Earl of Ravensworth, President, in the Chair.

iable to abrasion from shifting and moving of cargo, coals, &c.

The protection of the outsides of the bottoms of our ships from the destructive agencies of sea-water and dissolved gases may be said to have been attempted in two ways, by metallic and by non-metallic coatings.

So far, all attempts at metallic coatings have proved failures, and, as far as it is possible to judge, there is but small likelihood of their ever being made to succeed, because if zinc is used in order to protect the iron of the ship there must be galvanic action, and this action must take place evenly all over the surface of the iron plates, which means that the sheathing must be in uniform metallic contact with the iron, in which case the wasting of the sheathing would be so rapid that it would have to be renewed frequently, which, even leaving out the question of cost, is in many cases impossible.

Zinc is practically the only metal which could be used for this purpose, in order to place the plates of the ship in an electro-negative condition, and it is, therefore, to zinc that inventors have turned from time to time, the chief novelties introduced being the method of attachment. As far back as the year 1835, I believe Mr. Peacock tried zinc plates on the bottom of H.M.S. *Medea*, and in 1867 Mr. T. B. Daft again brought the subject forward: Sir Nathaniel Barnaby, Mr. McIntyre, and others, also suggesting various plans of attachment; whilst as late as last year Mr. C. F. Henwood read a paper at the United Service Institute, again strongly advocating zinc-sheathing as attached by his system.

Where the galvanic contact has been but small there the sheathing has had a certain life, but has afforded but little protection to the iron, and has gradually decayed away in a very uneven fashion; whilst in those cases where galvanic contact has been successfully made the ship has on several occasions returned from her voyage minus a considerable portion of the sheathing.

Another drawback to the use of zinc-sheathing is one which was found when it was used to coat wooden ships, and that is that zinc when in sheets, like every other metal, is by no means homogeneous, and that for this reason the action of sea-water upon it, leaving out of consideration galvanic action, is very unevenly carried on, the sheathing showing a strong tendency to be eaten away in patches, whilst the metal itself undergoes some physical change and rapidly becomes brittle.

Attempts have been made to galvanise the iron before the building of the ship; but Mr. Mallet showed as early as 1843 that this coating was useless when exposed to sea-water, as in from two to three months the whole of the zinc was converted into chloride and oxide, and that when, therefore, galvanising is used, care must be taken to protect the thin coating of zinc. This does not, of course, apply to fresh water, in which galvanised iron would answer very well, the rapid action being due to the salts in the sea-water; but even in this case the galvanising would have to be done after the plates had been riveted together, as any breaking of the surface would set up rapid wasting of the zinc, and it could, therefore, only be used on small craft.

Copper, tin, and lead have been proposed for coating ships, but these metals are electro-negative to iron, and would rapidly destroy the hull should any abrasion of the coating or damage to the insulating material take place.

The non-metallic coatings which are intended to do away with corrosion have been almost endless. At the present moment there are upwards of 30 in the market; whilst the patent list of the last 50 years contains an enormous number which were practically still-born.

They may be divided for convenience into—

(*a*). Oil paints.

(*b*). Pitch, asphalt, tar, or waxes.

(*c*). Varnishes, consisting of resins and gums dissolved in volatile solvents.

(*d*). Varnishes, containing substances to give them body.

(*e*). Coatings of cement.

And, before going into these in detail, it is necessary to consider the condition of the surfaces to which they will have to be applied, and the effect this will have upon them.

Air has the power of holding water vapour in suspension, the amount so held being regulated by the temperature; the higher the temperature the more can the air hold as vapour, whilst any cooling of the air saturated at the particular temperature causes a deposition of the surplus moisture. When a ship is scraped down to the bare iron in the dry dock, we have a huge surface of metal which varies in temperature much more rapidly than the surrounding air, and cools much more rapidly than the stone walls of the dock; as it cools so it chills the layer of air in immediate contact with it, and causes a deposition of the surplus moisture on its surface—a phenomenon known as the "sweating of iron"—and on to this moist surface the protective composition has to be painted. If now a rapidly drying varnish is put on, the rapid evaporation of the volatile solvent causes again another sudden fall of temperature — evaporation being always accompanied by loss of heat—and this fall of temperature again causes a deposition of moisture, this time on the surface of the protective, so that the coating is sandwiched between two layers of moisture, both of them probably acting deleteriously upon the resin or gum in the varnish, whilst the moisture on the iron also prevents adherence of the varnish to the metal. If, instead of a quick-drying varnish, the old-fashioned red lead and linseed oil protector had been used, the second deposition would not have taken place, but the sweating of the iron would have prevented cohesion, and, when dry, any rubbing of the coating would bring it off in strips.

The condition of the outer skin of a ship, when she is being coated with her protective composition, is one of the prime factors in the discrepancies found in the way in which compositions act. It being a very usual thing for a composition to give most satisfactory results on several occasions, and then, apparently under exactly similar circumstances, to utterly break down, and to refuse even to keep on. Too much stress cannot be laid upon the condition of the plates at the time of coating, and it is absolutely essential either to have a perfectly dry ship, or else a composition which is not affected by water.

When an old ship is broken up, you will often see on the backs of the plates the numbers which had been painted on them with white lead and linseed oil before the ship was built, and under the paint the iron in a perfect state of preservation, the secret being that the paint was put on while the plates were hot and dry.

Boiled linseed oil, mixed with red or white lead, is amongst the oldest of the protective compositions in use, but of late years has been but little employed, since it was proved by M. Jouvin, of the French Navy, and also in this country, that compounds of lead, when exposed by the wasting of the vehicle to the action of sea water are converted into chloride of lead, and this is rapidly acted on by the iron, depositing metallic lead and forming chloride of iron, the deposited lead carrying on the corrosion of the iron by rapid galvanic action. The drying of boiled linseed oil is due to the fact that it has in it a certain quantity of an organic compound of lead, and the drying properties are given to it by boiling it with litharge (oxide of lead), so that, even when red or white lead is not mixed with it, still lead compounds are present, and this action will go on to a lesser extent. When the boiled oil dries, it does so by absorbing oxygen from the air and becomes converted into a sort of resin, the acid properties of which also have a bad effect upon iron, so that protectives containing boiled oil are open to objection. Within the last two months a good example of the action of sea water on the bottom of an iron ship, coated with red lead,

has been afforded by H.M.S. *Nile*, which, after being painted over with coats of red lead, was allowed to remain for some months in Milford Haven, with the result that her bottom is very seriously corroded, and, on examination of specimens of rust taken from her, the crystals of metallic lead are in many cases easily identified.

If red lead is used, it can only form a ground-work for an anti-fouling composition which has to protect the red lead as well as the iron of the ship from the action of sea water, and when the anti-fouling composition perishes then serious corrosion must ensue.

The second class of protectives, consisting of tar and tar products, such as pitch, black varnish, and also asphalt and mineral waxes, are amongst the best protectives, the waxes especially not being affected by the sweating of the plates, and forming admirable coatings for the plates. Certain precautions, however, must be taken in the case of tar and tar products, both of which are liable to contain small quantities of acid and of ammonia salts; but if care be taken to eliminate these, and if it could be managed to apply this class of protectives hot to warm plates, the question of protection would be practically solved, bituminous and asphaltic substances forming an enamel on the surface of the iron which is free from the objections to be raised against all other protectives, that is, that being microscopically porous they are pervious to sea water.

The third class of protectives consists of varnishes formed by dissolving gums or resins in volatile solvents, such as spirit, turpentine, naphtha, fusel oil, &c., and such varnishes are open to several objections—in the first place, they are acted upon by moisture, which causes a deposition of the resins or gums as a non-coherent powder, and destroys the tenacity of the varnish. The amount of action which moisture has on such a spirit-varnish depends to a considerable extent upon the proportion of resin or gum to spirit, when the solvent is present in large quantities, and the resin in comparatively small; then the moisture has apparently little action; but it must be remembered that the drying of such protectives means the rapid evaporation of the solvent and concentration of the resin or gum, whilst the rapid volatilisation which is going on cools the hull of the ship, and causes deposition of moisture on the drying varnish with most disastrous results.

Another point which must be borne in mind is that no such varnish is impervious to gases and liquids. We are apt to think of a coating of varnish as being perfectly homogeneous; but, on examining it through a microscope, it is seen to be full of minute capillary tubes, which become gradually enlarged by the action of water, and finally result in the destruction of the varnish, whilst moisture and dissolved gases find their way to the metal and carry on corrosion. The application of several coats of varnish tends to diminish this evil, as in many cases the holes in the first coat will not correspond with the holes in the second, and so each succeeding coat will tend to make the protective more and more impervious. In using such varnishes, they must only be applied in favourable weather, and must be allowed to thoroughly harden before being brought in contact with the water.

In the fourth class we have varnishes of this kind to which body has been given by the addition of foreign constituents, generally mineral oxides; and this class is far preferable to the last, if the solvent used is not too rapid in its evaporation, and if care has been taken to select substances which do not themselves act injuriously upon iron or upon the gums or resins which are to bind them together, and are also free from any impurities which could do so.

At present the favourite substance used to give colour and body to such varnishes is the red oxide of iron, the colour of which effectually cloaks any rusting which may be going on under it. In using the red oxide for this purpose care should be taken that it contains no free sulphuric acid or soluble sulphates, as these are common impurities, and are extremely injurious, tending to greatly increase the rate of corrosion. The finest coloured oxides are, as a rule, the worst offenders in this respect, as they are made by heating green vitriol (sulphate of iron), and in most cases the whole of the sulphuric acid is not driven off as the heat necessary impairs the colour; this acid is often neutralised by washing the oxide with dilute soda solution, but very little trouble, as a rule, is taken to wash it free from the resulting sulphate of soda, which is left in the oxide.

A sample of exceptionally good colour intended for using in protective compositions was sent me a few weeks ago for analysis, and proved to contain no less than 15·3 per cent of sulphate of soda.

The best form of oxide of iron to use for this purpose is obtained by calcining a good specimen of hæmatite iron ore at a high temperature. When prepared in this way it contains no sulphates, but from 8 to 40 per cent of clay; if the percentage does not, however, exceed 12 to 18 per cent it is perfectly harmless.

Composition manufacturers can easily test their red oxide for themselves, to see if it contains soluble sulphates, by warming a little of it with pure water, filtering through blotting-paper, and adding to the clear solution a few drops of pure hydrochloric acid, and a little solution of chloride of barium (easily obtained at any druggist's). If a white sediment forms in the solution the sample should be rejected.

In a previous paper on the corrosion and protection of iron and steel ships, I pointed out that when such a varnish perished, the oxide of iron being left in contact with the iron plates, increased the corrosion going on at the surface of the metal, all oxides being electro-negative to the metals from which they are produced, and on that occasion I advocated the use of finely divided metallic metallic zinc, which can be obtained as an impalpable powder, in place of the oxide of iron, pointing out that such a composition would last as long as any varnish of this class, and that, when the varnish perished, as it must do after long exposure to sea water, then the metallic zinc would, on coming in contact with the iron, set up galvanic action; but that, instead of being electro-negative, as in the case of the oxide of iron, and causing corrosion of the plates, it would be electro-positive, and in consequence would protect them, being itself slowly oxidised, and so would give a fresh period of protection.

I hoped at the time that I had made it perfectly clear that the zinc would in no way act until both the anti-fouling and protective varnish had perished, and had become spongy and porous, and that the idea was a prolongation of the period of protection, the great point which has now to be aimed at; but the remarks made afterwards in several journals which were kind enough to notice my paper showed me that they had mistaken my intention, and supposed that the zinc was put in to at once create galvanic action, and predicted that if by any chance it did act, the hydrogen generated would blow the composition into blisters, and defeat its own purpose. I need hardly point out that nothing was farther from my intention, as zinc in fine powder would be acted on more rapidly than the dense metal in plates, and I have already pointed out that this is destroyed too rapidly by galvanic action to render it of practical use as a protective *per se*.

As to the hydrogen blowing off the composition, no gas could be generated until both the anti-fouling and protective coatings had been perished and rendered perfectly porous by the action of the sea water, a condition which would have permitted the free escape of the generated hydrogen, which, it must be remembered, will permeate through openings which other gases cannot pass through.

(To be continued).

The Use of Saccharine.—Ph. de Clermont.—The author recommends saccharine as an addition to chocolates, &c., intended for diabetic patients.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 28th, 1889.

Mr. William Crookes, F.R.S., President, in the Chair.

The President delivered an address, of which the following is an abstract:—

The number of fellows of the Society is 1650, of whom 36 are honorary foreign members; at the same period last year there were 1571 Fellows, of whom 37 were honorary foreign members.

140 Fellows have been elected during the year.

23 Fellows have died during the year:—Professor Brazier, R. Cartmell, John Collins, J. J. Coleman, Professor H. Debray (Foreign Member), W. F. Donkin, H. C. Foote, Peter Griess, A. N. Gow, John Horsley, J. M. Kavanagh, J. D. Perrins, Dr. David Price, F. G. Ree, J. Robinson, W. O. Senior, J. Storey, James Taylor, J. S. Topham, Thomas Ward, Dr. W. Wallace, G. J. Wishart, John Williams.

16 Fellows have withdrawn.

21 Fellows have been removed on account of arrears.

In the year 1888 there were 75 original papers published in the *Transactions*, occupying 895 pages, compared with 88 papers of 871 pages in 1887. The Abstracts in 1888 occupy 1351 pages, compared with 1159 in 1887. The number of Abstracts is 2470 compared with 2277 in 1887.

103 papers have been communicated to the Society this session.

The Library continues to increase, and every year is becoming richer in rare volumes and books of reference. The duplicate library for lending is also becoming increasingly useful. The following Table shows the present state of the shelves:—

	March 31st, 1888.	Addition in 1888-89.	Present state.
Volumes of systematic works	2780	142	2922
Volumes of journals ..	5119	355*	5474
Volumes of duplicate journals for circulation	941	143†	1084
Pamphlets	1410	16	1426
	10,250	656	10,906

The expenditure under this head for the current year is £308 5*s.* 6*d.*

I must now ask your attention to an event of which none of you can be ignorant, which, though not exclusively relating to chemistry, bears closely upon it and upon the future of British Science. I refer to the protest against the examination system in education which appeared in November last. That protest had long been in the air. For years past men who take the trouble to observe and to reflect have come to the conclusion that competitive examination is injurious to the individual, injurious to the race, and that it starves original research at the very root. They have convinced themselves that if we flag in scientific investigation, that if a large and increasing proportion of professorships and of leading positions in industrial establishments, both in the home kingdom and in the colonies, are filled by aliens, the fault lies mainly with our educational system. Men trained chiefly to pass examinations either in theoretical or practical departments cannot equal those who have been schooled in actual research, trained to accurately observe and draw correct inferences from facts. All the earlier protests were desultory, and calculated to produce no lasting impression; but the recent manifesto is the expression of the collective opinion of many earnest representative men and women. Hence it cannot be slighted as the mere outcry of a faction, a sect, a school, or an interest.

A most satisfactory feature is the adhesion to the protest of men who formerly were in favour of competitive examination as the test for entrance into the civil or military service of the State. Prof. Max Müller, of Oxford, frankly admits he now considers competition to be a mistake, and avers that the failure springs not only from the manner in which the system has been worked, but is involved in its very nature. But if this protest is to avail it must be energetically followed up, for I must repeat what I have before declared that the position of science in Britian is far from satisfactory.

Though the number of articles devoted to research in German transactions and journals exceeds those in our own publications, we must remember that the population of the German empire is greater than that of the United Kingdom by at least one-fourth; further, that the *savants* of Russia, of the Austrian empire, of Switzerland, of Holland, and Scandinavia largely select German journals as their medium of publication. Not a few English and American scientific men follow the same course. Hence, as regards quantity, our share in the world's scientific work is more considerable than appears at the first glance. Further, I think that if deficient in quantity English research excels in quality. If we do less detail work we furnish a larger proportion of generalisations and laws than most of our rivals. As the discoverers of laws and generalisations, Black, Boyle, Dalton, Faraday, Graham, Joule, Newton, Wollaston, and Young are household words in the laboratory—yet none of these men were the products of the examination system.

There is another evil against which I must strongly protest. I refer to the system of "sealed papers." Every one knows that on the Continent, more especially in France, it is common for anyone who has, as he thinks, approached the solution of some important question, to deposit a sealed sketch of his incomplete results with the president or secretary of some learned society. The sketch may lie *perdu* for years, until the author requests it may be opened and read before the Society. The practice arose from a desire that the author's priority should be guaranteed against others who might lay claim to his ideas. But priority can be quite as effectually secured by a brief preliminary notice read before some society or sent to some journal, the author thus reserving to himself the further investigation of the subject. Among men of honour such reservations are invariably respected. But the "sealed paper" system lends itself to something which borders unpleasantly upon fraud.

Suppose an investigator takes up some question, sees that it admits of two or more solutions, or that various hypotheses present themselves to him as possible. To work out the matter conclusively might require much time and trouble. He therefore writes out each hypothesis and incloses them separately in "sealed papers" duly numbered, carefully retaining copies. In process of time some other investigator, ignorant of what the first author has done, takes up the subject and works out one of these hypotheses to demonstration. So soon as his supplementary memoir is before the world the first investigator requests that the "sealed paper" No. 2 or No. 3 be opened and read. The new theory, laboriously considered and worked out, is found to have been anticipated, and the man who has really done the work is robbed of much of his credit. The seeming anticipator says nothing about the contents of other "sealed papers," in which he has proposed totally different hypotheses; these he now leaves to oblivion.

I think the Fellows of our Society will agree with me that a system which thus enables a man to reap the fruit

* Including 170 vols. *Dingler's Polytechnisches Journal.*
† Including 95 vols. *Dingler's Polytechnisches Journal.*

of another man's experiments does not deserve to be naturalised in England.

There is a further abuse to which attention may usefully be drawn. It sometimes happens a man of science will send an account of researches he has completed to two journals simultaneously, English or foreign, leaving each editor under the impression that he is the sole recipient of the communication. Or, still worse, a man reads a paper before our Society and sends it to some foreign journal, so that it may figure in print before it appears in the Society's *Transactions*.

To this subject I felt compelled to refer when I had the honour of addressing you last year. And you are now aware, your council declines to publish any memoir which has previously appeared in a foreign journal unless specially recommended by the Publication Committee and approved by the Council. The reasons for this resolution are not hard to seek. Not merely is the reputation of the Society, as the original channel of the researches in question, imperilled, or at least obscured, but a serious waste of time and labour is inflicted upon any one who needs to read up the literature of the subject. We, in England, are by no means the only sinners in this respect. It often happens that memoirs which have been read before the Paris Academy of Sciences reappear as "original matter" in certain French journals.

I cannot pass over a discovery made this season by Prof. Krüss concerning nickel and cobalt. As at first reported it seemed that these two metals might be eliminated from our text-books and that two or three new substances would take their place. Had this been the case it would undoubtedly have been one of the greatest steps in pure chemistry taken this century. It now appears that each of the two metals contains a common impurity which Prof. Krüss has been the first to detect and isolate. Nickel and cobalt thus purified will still retain their individuality, though their accepted properties, physical and chemical, will need careful revision.

In any case the discovery is most instructive, warning us how careful we should be to have firm ground under our feet. It is almost humiliating that two metals which have been subjected to infinite research and scrutiny should now be found to contain such a proportion of unsuspected impurity.

You are aware that at the ballots for the election of Fellows half an hour or more of valuable time is thus spent in a manner which, to say the least, is not very interesting. An attempt has been made to save time by taking the ballot in the library, after the meeting, but so many Fellows leave before the end of the meeting that the number remaining has not been found sufficient to meet the requirement of the bye-laws. Your Council have from time to time had this matter under discussion, and at their last meeting, on the 21st inst, it was resolved "that in future the balloting for Fellows be conducted by means of papers." The best manner of carrying out this resolution will be a subject for future arrangement.

A posthumous memoir on the compressibility of hydrogen, by the late Prof. Wroblewski, reminds us of the sad and untimely death of this meritorious and distinguished worker in physical chemistry. His death, as most of us doubtless are aware, was due to the frightful burns which he received from the overturning or explosion of a paraffin lamp. In the memoir in question Prof. Wroblewski treats of the compressibility of hydrogen at 99°, at 0°, at −103·5° (boiling-point of ethylen), and at −182·4° (boiling-point of oxygen) for pressures ranging from 1 to 70 atmospheres. From the results the following data were calculated:—Critical temperature − 240°; critical pressure 13·3 atmospheres; critical volume 0·00335. Hence it appears very doubtful whether M. Pictet or M. Cailletet really succeeded in liquefying hydrogen.

Last year I had the pleasure to announce that one of our Fellows, Mr. Newlands, had received the "Davy Medal" of the Royal Society for his splendid discovery of the Periodic Law of the Chemical Elements. I may also be allowed to state that to me, your President, the Royal Society has likewise awarded the same distinction for my Researches on the Behaviour of Substances under the influence of the Electric Discharge in a High Vacuum, with especial reference to their Spectroscopic Reactions.

Hence it has been suggested that I might not unprofitably claim your attention this evening for a History of the so-called Rare Earth, as they have been brought to light and discriminated by the aid of the Spectroscope.

[The continuation of the Address will be inserted *in extenso* in a future number of the CHEMICAL NEWS.]

Professor DEWAR proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Dr. GLADSTONE seconded the motion, which was carried by acclamation. The PRESIDENT briefly responded.

Dr. RUSSELL, the Treasurer, then gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3402; by sale of Journal, £365 3*s*. 3*d*.; and by dividends on invested capital, £344 4*s*. 3*d*. The expenses on account of the Journal had been £2350 5*s*. 11*d*.; on account of the Abstracts of Proceedings, £164 4*s*. 7*d*.; on account of the Library, £308 5*s*. 6*d*.; the total expenditure being £3429 18*s*. 3*d*. £500 had been invested in Metropolitan Board of Works 3½ per cent stock, and the balance in hand was £1833 10*s*. 6*d*., the balance at the corresponding period last year having been £1672 19*s*. 3*d*.

Professor THORPE moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Dr. PERKIN seconded the motion. Dr. RUSSELL, after replying, proposed a vote of thanks to the auditors, Messrs. R. H. Davies, Friswell, and Rideal; this was seconded by Dr. P. F. FRANKLAND, and acknowledged by Mr. FRISWELL.

Mr. J. NEWLANDS proposed a vote of thanks to the Officers and Council, which was seconded by Dr. J. VOELCKER, and acknowledged by Dr. ARMSTRONG.

Professor CLOWES moved that the thanks of the Fellows be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. COLLIE seconded the motion. Mr. GROVES and Dr. THORNE replied.

Messrs. Foster and E. W. Voelcker having been appointed Scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President—W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; Warren de la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—G. Carey Foster, F.R.S.; J. W. Mallet, M.D., F.R.S.; H. McLeod, F.R.S.; Ludwig Mond; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary—F. R. Japp, LL.D., F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Norman Collie, Ph.D.; A. H. Church; Frank Clowes, D.Sc.; Wyndham Dunstan; John Ferguson, M.A.; Charles W. Heaton; E. Kinch; H. F. Morley, M.A.; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

April 4th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Mr. Alexander Hill was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Waters Butler, Crown Brewery, Birmingham; Francis Ransom, Hitchin.

The following were elected Fellows of the Society:—Messrs. John Leigh Hoskyns Abrahall; James Aunal; Richard Douglas Bailey; T. D. Collis Barry; Frederick William Boam; Harry Broadbent; Edward Barnwell Cook; Francis Edward John Cridland; Alexander Archie Cunningham; Thomas Hill Easterfield; Joseph T. Freestone; William Frew; James Hall; Richard Ashworth Hoyle; Henry Richardson Hoyles; Herbert Ingle; Clement Joseph Leaper; George Cannon McMurtry; Christopher J. McNally, M.D.; James Bruce Miller; William Beattie Nesbitt, B.A.; George Thos. Wilkinson Newsholme; John Charles Platts; Charles Proctor; Arthur Avery Read; Ernest Reckitt; Duncan Taylor Richards; Richard Wrightwick Roberts; Thomas Alexander Shegog; Henry Simmonds; John William Slater; Henry Charles Anslie Vine; Walter Arthur Voss; William John Waterhouse; Patrick Alexander Wier, M.B.; John Tsawoo White; Charles Wood; Mortimor Woolf.

The following papers were read:—

33. "*The Rate of Dissolution of Metals in Acids.*" By V. H. Veley.

When the rate of evolution of a gas is taken as the measure of the amount of interaction between metals and acids, the result is due to a variety of causes, each one of which is variable at any moment of time, and its peculiar effect not susceptible of mathematical analysis. Among the varying conditions are the surface of the metal exposed, the local rise of temperature, the rate of diffusion of the metallic salt formed in the acid liquid, and the rate of its removal by the gas-bubbles. In the present research metallic spheres, by various mechanical devices, were rolled about continuously and regularly within the acid liquid, and the products of the changes continuously removed from the immediate neighbourhood of the metal. The dissolution of copper in a solution of potassium bichromate acidified with sulphuric acid was investigated as affording a case in which no gas is evolved as such. The dependence of this action on the conditions of (i.) temperature, (ii.) proportion of sulphuric acid, and (iii.) proportion of potassium bichromate, is illustrated by various series of experiments.

(i.) As regards temperature, it is shown that if this be varied between 21° and 41° in an arithmetical proportion, the amount of chemical action varies in a geometrical proportion: in this respect the change is perfectly analogous to several others quite different from it and from one another. Attention is drawn to this relation as common to a number of chemical changes, and to the causes on which it is probably dependent. (ii.) On varying the amounts of sulphuric acid in an arithmetical proportion within the limits of 41·3 and 23·5 grms. per litre, the amount of change also varies in an arithmetical proportion. (iii.) The amount of change is at first considerably increased by increase of proportion of potassium bichromate, but the effect gradually diminishes almost to *nil*, at which point the bichromate can be considered as so much inert material; the amounts used varied from 22·1 to 66·3 grms. per litre.

34. "*Note on the Interaction of Metals and Acids.*" By Henry E. Armstrong.

When a metal forming an element in a voltaic couple is dissolved, the rate of dissolution is in accordance with Ohm's law, C=E/R: and this should apply also to the case in which a metal is dissolved without any precaution being taken to arrange it as an element of a couple, as the action is conditioned by the formation of, and takes place within, "local circuits." The changes attending the dissolution of metals may, therefore, in a certain sense, be said to be purely electrical in the first instance; yet, within recent years, it has been argued by various chemists that the phenomena are only in part electrical and in part chemical—whatever this may mean. The author discusses the various phases of such changes, and criticises the conclusions arrived at by Spring and Aubel and others.

Discussion.

Referring to Mr. Veley's experiments, Dr. Armstrong expressed the opinion that the results were in no way commensurate with the labour expended in obtaining them; although by introducing bichromate polarisation by hydrogen had been prevented, its use had introduced complications which made the analysis of the results impossible; in fact, the information likely to be obtained from such experiments was not of the kind required in the present state of chemical science. Thus, the proof obtained that a copper sphere dissolved uniformly in a mixture of sulphuric acid and bichromate was but a proof of the efficiency of the stirring apparatus: such would necessarily be the case, as the values of E and R remained almost unchanged throughout the experiment, owing to the relatively small proportion of the agents used up.

Mr. Veley, in the course of a reply in which he attempted to justify his position, mentioned that he had had occasion to verify Dr. Russell's observation that silver is not dissolved by nitric acid, to which reference had been made, and stated that in experiments with copper and nitric acid he had observed that the action took place at first more slowly, and only attained a maximum rate when a certain small amount of nitrate was formed.

Dr. Armstrong remarked that this was a really important observation, proving that the dissolution of copper in nitric acid was dependent on the presence of a third substance—perhaps cupric nitrate. The discovery of the exact conditions which determine any particular chemical change is at the present time of great importance, and investigations establishing these were much required; it was useless, however, to study cases in which complications instead of simplifications were introduced, as even the changes which apparently were of the simplest kind, were probably but the end results of more or less complex series of successive or simultaneous changes.

35. "*A Zinc Mineral from a Blast-Furnace.*" By J. Tudor Cundall.

The author has examined a mineral found in cavities of the wall of a blast furnace at Mostyn, in North Wales; it crystallises in white to yellow translucent tufts, of the relative density 5·60. Analysis gave results which show that it is impure zinc oxide:—

	ZnO.	Pb.	S.	SiO_2.	FeO.
I.	97·96	1·02	0·39	0·61	0·39
II.	98·97	0·95	0·10	trace	trace

It was examined crystallographically by Mr. A. Hutchinson, who found that the crystals belong to the rhomboidal system, and exhibit combinations of the hexagonal prism and pyramids with the basal plane; two new forms were also noted, viz., the rhombohedron $r\{100\}$ and the hexagonal pyramid $h\{21, 13, 17\}$.

Faraday Lecture.

The Faraday Lecture will be delivered on June 4, by Professor Mendeleeff, in the Theatre of the Royal Institution. The Fellows of the Society will entertain the Faraday Lecturer at a dinner at the Holborn Restaurant on the following evening.

PHYSICAL SOCIETY.

April 13, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MESSRS. J. E. Dowson, W. M. Mordey, E. A. O'Keefe, C. Priest, A. Siemens, and W. B. Willans, were elected members.

Mr. SHELFORD BIDWELL, F.R.S., showed "*A Lecture Experiment Illustrating the Effect of Heat on the Magnetic Susceptibility of Nickel*," and "*An Experiment Showing an Effect of Light on Magnetism.*"

In the first experiment a piece of nickel was attached to one side of a copper pendulum bob, which was held out of the vertical by bringing the nickel in contact with a fixed magnet. On placing a spirit-lamp flame below the nickel the bob was (after a short time) released, and oscillated until the nickel had cooled, when it was again attracted and the operation repeated itself.

The second experiment had been recently shown before the Royal Society. One end of an iron bar, which had been magnetised and then de-magnetised, was placed near a magnetometer needle. On directing a beam of light on the bar an immediate deflection of the needle resulted, and on cutting off the light the needle promptly returned to near its initial position. The direction of magnetisation induced by the light is the same as the previous magnetisation, and the bar seems to be in an unstable magnetic state. That the effect is due to light and not heat the author thinks is rendered probable by the suddenness of the action.

The PRESIDENT said he had tried the experiment himself, and failed to get any effect, but after seeing the arrangement of apparatus used he believed his non-success due to the comparatively great distance between his bar and needle.

A MEMBER asked if the results were different for different coloured rays, and

Prof. S. P. THOMPSON enquired whether the magnitude of the effect varied with the intensity of illumination, as in selenium, and also if any change was produced by altering the direction of vibration of the incident light.

Mr. G. M. WHIPPLE wished to know whether any difference was produced by blackening the bars, and, as bearing somewhat on the same subject, mentioned an induction magnetometer in which an iron bar used was demagnetised by plunging in hot water. The results obtained were very irregular after the first magnetisation, and this may have been due to the instability shown to exist by Mr. Bidwell's experiment.

In reply, Mr. BIDWELL said red light produces most effect and blackening the bar makes the action much slower. As regards selenium the character of the effect is similar, but he believes the causes to be different. Polarised light produces no change. In answer to Prof. Herschel he said that any part of the bar is sensitive to light, and showed that illuminating both sides of the bar increased the effect.

Mr. G. M. WHIPPLE read a "*Note on the Dark Flash Seen in Some Lightning Photographs.*"

After expressing his dissent from the explanations offered in the report of the Lightning Flash Committee of the Meteorological Society and Prof. Stokes respecting "Ribbon Lightning" and "Dark Flashes," the author described some experiments he had made on the subject. Ribbon lightning he conceives to be an effect produced by taking the photographs through windows, and to test this lines on a blackboard were photographed: 1st, direct; 2nd, through good plate-glass placed obliquely; and 3rd, through window-glass; the result being that double, triple, and ribbon flashes were closely imitated. As regards "Dark Flashes," the author believes the appearance due to the prints being taken in oblique light, and to be produced by successive reflection from the reduced silver forming the dark line on the negative and the upper surface of the glass of the negative.

Prof. PERRY suggested that this might be easily proved by examining a negative the prints from which show the dark flash.

Mr. BAILY pointed out that if the explanation given was correct the dark one should be parallel to the bright one, and this he understood was not always the case.

Mr. BOYS remarked that one dark flash exhibited minute wriggles not seen in the bright one, and

Mr. C. V. BURTON thought these might be due to irregularities in the upper surface of the negative.

Dr. GLADSTONE said he was not satisfied with Prof. Stokes's nitrous oxide explanation, but thought the phenomena may be due to some kind of reversion. He also mentioned that a negative might probably be obtained from Mr. Shephard, of Westbourne Grove.

As regards "Multiple Flashes," Mr. BOYS said he had often seen seven or eight flashes traverse the same path in rapid succession.

On the motion of the PRESIDENT the discussion was adjourned until next meeting, when Mr. Whipple hopes to exhibit the negative referred to, together with photographs of his experimental dark flashes.

"*On Quartz as an Insulator.*" By Mr. C. V. BOYS, F.R.S.

In making quartz fibres the author observed that the ends of fibres broken during the shooting process coiled up into screws and projected themselves against anything brought in their vicinity. After a short time they released themselves and sprang back to their original position. This could be repeated indefinitely, and the only explanation he could think of was that the fibres were electrified. If so, then to exhibit such phenomena the insulating properties of quartz must be very great, and experiments were shown to demonstrate this deduction. A small pair of charged gold leaves were suspended from a short quartz rod in a moistened atmosphere, and the deflection fell one-fourth the original amount in about five hours. A clean glass rod under the same conditions would discharge the leaves in a few seconds. Dipping the quartz into water did not seem to diminish its insulating properties, and ordinary chemicals produce no permanent prejudicial effect. The author considers that quartz will be very useful in electrostatic apparatus, for the troublesome sulphuric acid may be dispensed with.

"*On a Refraction Goniometer.*" By Mr. A. P. TROTTER

The goniometer, which was designed when determining the figure of a refracting surface to effect a special distribution of light, is practically a movable four-bar linkwork representing the figure given in Deschanal, p. 924; two of the bars are parallel to the incident and emergent rays, and the other two normals to the faces of the prism. By its means the angle of a prism to produce a given deviation, when the index of refraction and angle of incidence are known, can be readily found. A series of curves expressing the relation between incidence and deviation for prisms of various angles were shown, and the same curves show the minimum deviation and limiting angle for prisms of all angles represented. The author thinks the instrument will be useful in physical laboratories for adjusting optical apparatus and for the calculation of lighthouse and other polyzonal lenses, Fresnel prisms, &c.

Prof. HERSCHEL said he found a wooden model, illustrating the relations between the angles of incidence and refraction very useful in teaching, and

Mr. BLAKESLEY sketched an arrangement of links and cords devised for the same purpose.

Mr. BOYS considered that all such relations were best on a slide rule.

"*A Note on Apparatus to Illustrate Crystal Forms*," by Prof. R. J. ANDERSON, was read by Prof. PERRY.

The apparatus is constructed of cords, pulleys, and weights, arranged to produce the required figure when in equilibrium. By increasing or decreasing some of the

weights the corresponding axes of the crystal forms can be lengthened or shortened, and the passage from one system to another effected. In one arrangement the forces may be divided or united, and the pulleys are carried by rings capable of rotating on different axes. By this apparatus the various conditions are said to be beautifully illustrated, and methods of deriving the oblique from the rectangular systems are shown in photographs which accompany the paper.

NOTICES OF BOOKS.

The Principles of Empirical or Inductive Logic. By John Venn, D.Sc., F.R.S., Fellow and Lecturer in the Moral Sciences, Gonville and Caius College, Cambridge. London: Macmillan and Co.

The work before us, though approximating to the "System of Logic" of John Stuart Mill, differs from it so decidedly, and in many points so advantageously, that it will not be regarded as an *Ilias post Homerum*. Attention must first be called to the introduction of the term "empirical" into the title. By this the author, as he tells us, wishes to "emphasize his belief that no ultimate objective, certainly such as Mill, *e.g.*, seemed to attribute to the results of induction, is attainable by any exercise of the human reason." Dr. Venn aims at being constructive rather than critical, but his treatise will be unavoidably compared with that of Mill, already referred to. It will, we think, be seen that he possesses a mind more imbued with the spirit of scientific inquiry than was that of his predecessor. This statement will doubtless surprise some of our readers. But on careful examination we shall find that Mill was not a man of Science. His own training had been exclusively classical and literary, and to the last he sought to uphold the predominance of literature in education. No man of Science could ever have penned his well-known outbreak against the influence of heredity in the genesis of character.

Like several of his predecessors, Dr. Venn discriminates very closely between Science and Art. As he puts it:—"By Science may be understood a coherent and methodical body of generalisations about matters of fact; by Art, a similar body of rules for securing some end or class of ends. The former deals with what is; with what exists in great part irrespective of our wishes. The latter deals rather with what ought to be, or with what is wished for; wished for, it may be, by the speculator or by others as represented and interpreted by him." We fear, however, that here Dr. Venn will have lost his labour, and we refer to his opinion more in the hope of showing that so judicious a thinker adheres to the protest against the popular abuse of the terms Science and its paronyms, than in any hope of widely influencing the British public.

As inductive methods the author accepts with certain reservations the four processes recognised by Mill, viz., the methods of difference, of concomitant variations, of agreement, and of the joint method of agreement and difference, or, as he more happily calls it, the method of exclusions. Concerning the method of difference, he remarks that it is a means rather of verification than of discovery. He points out, too, the great practical difficulty in its application, that of being certain that no other antecedent save those we have taken into consideration has slipped in. This point requires care, even in physical and chemical inquiries. In biology the method becomes one of grave difficulty, and in social science it is scarcely manageable at all. Another precaution which he justly insists upon is that the step of omitting or inserting some one antecedent shall not involve any collateral effects.

The method of concomitant variations turns, of course, on the partial exclusion of some antecedent which cannot be entirely eliminated. Some of the instances here given of the unsatisfactory character of this method cannot be considered fair. They prove merely its limited applicability. The partial closing of a polluted drain could not be expected to throw any light upon the question whether such drain were a main factor in producing a local epidemic. The method of agreement Dr. Venn considers as merely suggesting the directions for experiment. The method of exclusions deals with cases in which the supposed cause and effect are both absent, and on this, where available, a great weight is laid. The author, however, emphasizes the consideration that the four inductive methods just discussed involve no appreciation of quantity. "Accurate measurement, in fact, forms the essence of true science." If this proposition is correct biology and psychology are not true sciences, and to beings possessing merely human faculties scarcely ever can become so. Who can say whether there then is more or less life in a child than in an adult, in a polype than in an eagle? To such questions diametrically opposite answers, both alike incapable of demonstration, might be given and maintained with profuse inkshed. Considerations relating to measurement have been, it is here pointed out, omitted by Mill and discussed at great length by Jevons.

The chapter on the data of geometry is very instructive. The author does not admit, with Mill, that lines and planes are not mere boundaries, but a something almost approaching material entities, formed by gradually "fining down" a thin sheet of paper or a spider's thread.

Explanation and verification are treated as steps towards the methodisation and establishment of our knowledge of Nature. It is pointed out that a certain satisfaction is reached by the mere taking a fact out of its isolated condition and including it under some general head. This chapter is one of the most valuable in the whole work, and deserves very careful study.

Passing over the section on a universal or perfect language, we come to a chapter on the extensions of our general powers of observation, especially by aiding or intensifying the powers of our own organs, such as in the case of sight, is effected by means of the microscope. Quoting Hooke, he calls attention to the improvement of smell, which is certainly of far greater value than hearing in our inquiries into Nature. What an advance would ensue, both in our chemistry and our biology, if we could gain olfactory powers equal to those of the bee and the wasp, which accept beet-root sugar only as a *pis aller* in the absence of cane-sugar, and which reject Fahlberg's saccharin as an insulting simulacrum!

The work before us must be accepted as preferable to Mill's in every respect save one, *i.e.*, the character of the illustrative examples. Concrete instances would be far more readily grasped than symbolic ones, such as that of the bells ringing in different rooms, A, B, C, D, &c.

Electro-Deposition: A Practical Treatise on the Electrolysis of Gold, Silver, Copper, Nickel, and other Metals and Alloys, with Descriptions of Voltaic Batteries, Magneto- and Dynamo-Electric Machines, Thermopiles, and of the Materials and Processes used in Every Department of the Art, and Several Chapters on Electro-Metallurgy. With numerous Illustrations. Third Edition, Revised, Corrected, and Enlarged. London: Crosby Lockwood and Son.

The number of persons who practise the electro-deposition of metals in the widest sense of the term falls scarcely below those who concern themselves with photography. In addition to thousands of amateurs there are a multitude of manufacturers who have occasion to make use of the art on a more or less extensive scale in the course of their business. And as Mr. Watts's work is undoubtedly the best modern treatise on the subject in the English language we need feel little surprise that the

second edition (1886) has been already succeeded by a third.

A very severe critic might take objection to the use of the term "electrolysis" on the title-page. Everyone can understand the electrolysis, *i.e.*, the decomposition by electric action, of the salts or alloys of gold, silver, &c. But the electrolysis of the metals themselves would be indeed a novelty.

We find here three chapters on electro-metallurgy, an art confounded by many persons with electro-deposition, but which the author correctly defines as the extraction, separation, and refining metals from ores by electric action. Among its many and multiplying operations we find here an account of the Cowles electric smelting process as now applied in the production of aluminium and its alloys. It is mentioned that at the Cowles Company's works at Stoke-upon-Trent a dynamo having a guaranteed capacity of 402,000 volts is about to be put down. He suggests that our government might do well to employ aluminium-bronze for heavy artillery. Its tensile strength is to that of steel as tensile strengths of 100,000 and 130,000, as against steel plates 81,000 and cast-steel 63,000.

The most important additions to this edition are compressed in an appendix, and include methods for depositing platinum, aluminium and its alloys, and cobalt; the removal of the tin from waste tinned iron, &c. A section on poisoning includes, of course, merely those substances with which the electro-depositor is likely to form unpleasant acquaintance in his labours. The author mentions that he once "inadvertently swallowed a quantity of old gold solution, which he had placed in a tea-cup for experimental purposes, in mistake for some coffee without milk which it was his custom to drink when at work in his laboratory." We cannot help calling this a most imprudent custom. No liquid should ever be consumed in laboratories, colour-shops, or other rooms in chemical manufactories, dye and print-works, &c. We have observed very serious accidents result from the neglect of this caution.

The table of atomic weights is not free from error, as that of platinum is still given as higher than gold.

There is a useful bibliography of works on electro-deposition, and the index is commendably copious.

CORRESPONDENCE.

ESTIMATION OF COBALT AND NICKEL.

To the Editor of the Chemical News.

SIR,—Referring to the paper "On Cobalt and Nickel Peroxides and on the Volumetric Determination of these Metals," translated from the *Comptes Rendus* into the CHEMICAL NEWS (lix., p. 183), the author, A. Carnot, is evidently unaware that English investigators have preceded him in his subject, and whose results are not wholly in harmony with his. It would not be inferred, for instance, from Bayley's work "On the Higher Oxides of Nickel and Cobalt" (CHEMICAL NEWS, vol. xxxiv., p. 81), that Fleischer's process could, by any practical modification, be adapted to the accurate volumetric estimation of nickel: yet, according to M. Carnot, nickel peroxide precipitated with potash and bromine is of stable and definite composition, and representable by the formula Ni_2O_3. Now Bayley shows—and I have in part corroborated his work (CHEM. NEWS, vol. lvi., p. 27)—that nickel peroxide obtained as above may, according to the proportion of chlorine or bromine, the temperature of precipitation, and length of time of subsequent boiling, if any, have any proportion of oxygen from Ni_3O_4 to Ni_3O_5.

To touch on one more of M. Carnot's statements:—"The brown oxide obtained on precipitating cobalt by oxygenated water and potassa at a boil presents the exact composition of a sesquioxide, Co_2O_3." I have not the slightest doubt that the author is in error on this point. Scores of careful experiments have satisfied me that the formula $Co_{13}O_{19}$ is nearer the truth, and that, again, only so far that as a basis for the volumetric estimation of cobalt, the results may differ by four per cent of the quantity of cobalt taken.—I am, &c.,

NORMAN MCCULLOCH.

Laboratory, Clyde Iron Works
(by Tolcross), Glasgow,
April 22, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Journal de Pharmacie et de Chemie.
Vol. xix., No. 7.

Assay of Smoking Opium (Chandoo).—M. Lalande.—The author finds that the ordinary procedures used for the determination of morphine should be modified for the examination of chandoo. He weighs out 10 grms. chandoo, 4 grms. slaked lime, and mixes them intimately with 100 c.c. of distilled water. He stirs the mixture from time to time and filters after the lapse of an hour. He receives 64 c.c. of the filtrate in a round wide-mouthed stoppered flask, adding 1 grm. ammonium chloride and 10 c.c. of washed ether. The flask is stoppered, carefully shaken to dissolve the salt, and the bases precipitated at the outset, and the whole is set aside for four days. The ether is then decanted, renewed, decanted afresh with a Robiquet's apparatus, and the liquid is filtered through a filter without folds. The crystals, carefully detached from the sides of the flask, are triturated with 20 c.c. of water, which serve for washing the filter, then with 20 c.c. of alcohol at 30 per cent, by means of which they are collected upon the filter. They are dried, washed with 20 c.c. of chloroform in four applications, dried at 100°, and weighed. The weight is the morphine in 6 grms. of chaudoo.

New Process for Detecting the Presence of Foreign Colouring-matters in Wines.—A. Pagnoul.—The author uses as a reagent the standard soap-liquid used in determining the hardness of waters. Of this liquid 5 c.c. are placed in a small test-tube with an equal volume of distilled water. From 10 to 20 drops of the wine in question are added and the whole is mixed by inverting the tube. With a natural wine the liquid remains colourless, but it is coloured if some foreign colouring-matter is present.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 6. March 20th 1889.

The Development of Chlorine during the Decomposition of Chlorates by Heat.—W. Spring and E. Prost.—The authors have submitted to the action of heat the chlorates of K, Na, Ba, Al, Ag, Cu, Zn, Pb, and Hg, heating them in boats of platinum or porcelain firstly alone, moist or dry, then in contact with carbonic, silicic, and phosphoric anhydrides and phosphoric acid. In each case the manner of heating has been modified, being either abrupt or gradual, and lastly, currents of dry air have been let circulate slowly or rapidly. The proportion of chlorine evolved varies much with the nature of the

chlorate and with the conditions of the experiment. It is larger in case of the chlorates of feeble bases and in presence of an anhydride capable of forming a salt with the base of the chlorate. If we also take account of the notable augmentation of chlorine when the heat is abrupt we are led to think that the chlorine disappears from among the gaseous products only if it has time to react with the base which has been set at liberty for an instant at least. These facts seem to be explained if the production of oxygen is not an immediate but an indirect result of the decomposition of the chlorates. These salts are split up at first, like the carbonates and nitrates, into a base and an anhydride. The chloric anhydride is then decomposed in turn into oxygen and chlorine, which latter reacts upon the base. These facts seem to show that if the salts are not actually formed by the juxtaposition of bases and anhydrides these tend to reappear when the molecule is split up under the influence of heat.

The Trivalence of Aluminium, and on a New Compound of this Metal.—Alphonse Combes.—The author seeks to show that the compounds of aluminium have the general formula AlR_3. The novel aluminium compound is the acetylacetonate, $Al(C_5H_7O_2)_3$.

Colouring-matters derived from the Tetrabenzylic Ether of Benzidine.—Albert Colson.—M. Colson describes the isolation of the dibenzylic ether of hydroquinone and the formation of the nitro-derivative. If this substance is reduced by zinc in an alkaline solution it gives a yellow compound, fusible at 140°, and a small quantity of a base soluble in alcohol, which, in contact with dilute hydrochloric acid, deposits the hydrochlorate of a benzidine which takes a red colour in the air. This benzidine, if transformed into a tetrazo-derivative, combines in the cold with salicylic acid, sulphonaphthol, and other phenols, yielding colouring-matters which combine direct with cotton in an alkaline bath. But these colours have not the brightness of the dyes obtained with the tetramethylic or tetraethylic ether of benzidine.

The Danger of Using White Lead in Lace.—Ph. de Clermont.—The author mentions that certain kinds of lace ("Point d'Angleterre") are got up with lead carbonate to an extent calculated to injure the health of the wearers, and to be completely spoiled on contact with any gas or vapour containing sulphuretted hydrogen.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 1.

The Degree of Accuracy of the Tests for Silver.—H. Rossler.—For the particulars of these two papers the reader is referred to the *Zeitschrift fur Angewandte Chemie.*

Systematic Procedure for Examining Quinine Sulphate on Hydrochlorate.—C. Hielbig.—This paper will be inserted in detail as early as possible.

Determination of Resin Oils in Mineral Oils.—H. Demski and Th. Morawski.—The authors reject the methods of E. Valenta (optical dextro-rotatory power, high iodine values, and solubility in glacial acetic acid) as not suitable for quantitative determinations. They find that in American and Gallician oils an admixture with resin oil exceeding 35 per cent may be detected by the complete miscibility of the sample with acetone. In Wallachian and Caucasian oils this phenomenon does not occur with less than 50 per cent of resin oil.

Bunsen's Determination of Urea, with Reference to the Nitrogenous Extractive Matters, and to the Salts of Ammonium.—K. Bohland.—The author proposes a modification of the improvement on the Bunsen process as suggested by himself and Pflüger.

Detection of Indican in Urine by Means of Chloroform and Chloride of Lime.—L. Renault (*Archiv der Pharmacie*).—In presence of iodides the reaction may be masked, but, in such cases, a subsequent addition of sodium thiosulphate converts the iodine into hydriodic acid and allows the colour of the indigo to be distinguished.

The Application of the Furfurol Reactions for the Detection of Biliary Acids and Carbohydrates in Animal Fluids.—This memoir does not admit of useful abstraction.

Determination of Albumen in Urine.—Ch. Lecerf (*Archiv der Pharmacie*) boils 50 c.c. of the sample with sodium sulphate and acetic acid, and determines nitrogen in the precipitate by Kjeldahl's process. He calculates the albumen by multiplying the nitrogen by 6·24.

Examination of Flesh for Caustic Alkalies.—Vitali.—The author digests the masses under examination with eight volumes of absolute alcohol, and washes out the residue with alcohol. A small quantity of the alkaline liquid is tested for caustic alkali with mercurous chloride.

Detection of Oxalic Acid in Cases of Poisoning.—D. Vitali (*Annali di Chimica*).—Absolute alcohol extracts part of the acid out of a mixture of flesh and oxalic acid. It may then be precipitated as ammonium oxalate by adding ammonia. This deposit is dissolved in water, precipitated with lead acetate, the precipitate of lead oxalate is decomposed by sulphuretted hydrogen, and free oxalic acid is crystallised out of the solution.

A Conspectus of the Ptomaines and Leukomaines at Present Known.—The reader is referred to the *Pharm. Central Halle* (29, 336).

Reactions of Physostigmine (Eserine).—W. Eber (*Pharm. Zeitung*).—The most sensitive reactions are with gold chloride (reduction), and potassium-bismuth iodide, and potassium-zinc iodide, the latter of which indicates 0·000001 grm. of physostigmine. Platinum chloride does *not* give a precipitate.

The Atomic Weight of Silicon.—T. E. Thorpe and J. W. Young.—From the *Journal of the Chemical Society.*

MEETINGS FOR THE WEEK

MONDAY, 29th.—Medical, 8.30.
TUESDAY, 30th.—Royal Institution, 3. "The Italian Renaissance Painters; their Associations," by Jean Paul Richter.
—— Society of Arts, 8. "The Northern Waterway to Siberia," by Capt. Wiggins.
—— Institute of Civil Engineers, 8.
WEDNESDAY, May 1st.—Society of Arts, 8. "Secondary Batteries," by W. H. Preece, F.R.S.
—— Royal Institution, 1,30. Annual Meeting.
THURSDAY, 2nd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "The Science of Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
—— Sanitary Institute, 8. "Rural Epidemics, by Dr. Bushell Anningson.
—— Chemical, 8. "Thiophosphonyl Fluoride," by Prof. Thorpe, F.R.S., and Mr. Hambly. "The Boiling-point of Potassium and Sodium," by G. P. Penman, B.Sc.
FRIDAY, 3rd.—Royal Institution, 9. "On Aluminium," by Sir Henry Roscoe, F.R.S.
—— Society of Arts, 8. "The Karun as a Trade Route," by Major-Gen. Sir R. Murdoch Smith.
—— Geologists' Association, 8.
SATURDAY, 4th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1536.

EXAMINATION OF FEED WATER FOR STEAM-BOILERS.

By THOMAS T. P. BRUCE WARREN.

Although water used for any special industry may require peculiar methods of treatment to render the same better adapted for certain manufactures, the same latitude cannot be extended to a boiler-supply. In this case the main points to be provided for are the prevention of scale and corrosion. Scale, resulting from carbonates of lime and magnesia, may be guarded against by the ordinary process of softening by means of lime. Sulphate of lime cannot be removed in the same way, but by using caustic soda and lime together its removal may be made complete. Corrosion arises from the liberation of hydrochloric acid from magnesium chloride, and is quite as serious as scaling. Magnesium chloride may not exist as such in the water, but we cannot be sure that by heating a soluble magnesian salt with a soluble chloride in a steam-boiler we do not bring about a reaction which results in its formation.

Great stress is laid on the hardness of water, but it seems to me that if the excessive hardness of water is due to freely soluble salts of lime and magnesia which cannot result in scaling or corrosion, we are scarcely justified in condemning it as a boiler supply, where we have not the choice of a supply of a purer type of water, unless at a great cost.

Assuming that we have a water yielding a large total, in the way of soluble solids, free from magnesium chloride and calcium sulphate, it would be interesting to know what is the extra consumption of fuel required to hold a large quantity of soluble substances in solution. I am not aware that this subject has been considered by any writer on water analysis, whilst to a manufacturer, the capacity for heat of his boiler supply when concentrated by the evolution of steam, is of paramount importance. We know that concentrated saline solutions have a boiling-point considerably over 100° C.; the temperature of the escaping steam is 100° C. Admitting the principle of the conservation of energy, there must be a consumption of heat which is not refunded in the dynamical form of work by the engine. No doubt this is a simple problem in chemical physics; the mere fact of a substance dissolving absorbs energy, and the re-crystallisation again absorbs energy. It does not follow that the total energy in each case is additive, but in striking a balance as to the consumption of fuel, we can hardly come to the conclusion that we entail no loss. The higher the temperature is above that required for solution the less is the loss of heat relatively, but on cooling down we probably cannot recover the total energy given out by the coal in burning.

In examining a water for steam boilers, the temporary hardness is of great importance, as it furnishes us with the data for roughly calculating how much lime is required to take up the carbonic acid, so as to render the carbonates of lime and magnesia insoluble. According to Prof. Frankland, one ounce of lime to 700 gallons of water for each degree of hardness will, *approximately*, do all that the lime economically can perform. It is perfectly true that lime will precipitate many salts of magnesia, but it is tedious and troublesome to deal with in practice. It is better to do this by means of sodic hydrate or carbonate; the hydrate may be used with the lime at one operation; the carbonate, if used, should be added after the lime has well acted upon the water. We may thus make sure of removing magnesium chloride. The water residue is carefully heated in a platinum dish to 127° to 130° C., covered with a watch glass which has been moistened with a little acidified nitrate silver solution, which will become rapidly turbid if any hydrochloric acid is given off. More soda is to be added to the water, until no turbidity is detected.

The estimation of the chlorides may be made in the ordinary way with the hard or softened water. A measured quantity of the water is evaporated to dryness, and the residuum heated to 127°—130° C. for some time; the residuum is dissolved, and the chlorine again estimated. The loss of chlorine will show that magnesium chloride has not been totally removed. If the chlorides of lime and magnesia have been removed the dry residuum will be considerably less hygroscopic.

It is an important matter to be able to find out readily how much lime or soda has been added in excess. A measured quantity of the softened water is coloured with a few drops of solution of phenolphthalein; the hard water is then run in until the colour barely vanishes; the free carbonic acid is taken up so long as lime or soda is in excess, and consequently does not mislead in the colour reaction.

ON THE INFLUENCE OF COPPER UPON THE DETERMINATION OF IRON IN FERRO-ALLOYS.

By T. W. HOGG.

The ease and rapidity with which most iron alloys are decomposed by dilute hydrochloric or sulphuric acid and then oxidised by means of a standard solution of bichromate of potash, render such a method for the direct determination of iron of considerable technical importance, and it is well known that as a general rule the results so obtained are fairly accurate.

As our standard text-books do not caution the operator against any occasional source of error it is very important to remember that when examining strange alloys, if any of them should contain copper, the results obtained by the above method become quite erroneous. When such an alloy is decomposed by the dilute acid the whole of the copper remains behind in the metallic state and does not pass into the solution, as might be supposed. It is now that the accuracy of the process begins to be seriously interfered with, for as soon as the standard solution of bichromate is added and there is present iron in the ferric state, then the finely-divided copper gradually reduces this back to the ferrous condition; the iron determination will thus come out too high, and the extent of the error will depend upon the quantity of copper present and the rapidity with which the titration has been conducted.

That the error so introduced may sometimes be a serious one will at once be evident when it is remembered that there are many published analyses of spiegeleisen showing considerable quantities of copper, and I have myself in one case found as much as 0·65 per cent. I have also met with several specimens of foreign tool and casting steels and other special iron alloys containing large quantities of copper, in some cases occurring as an impurity and in others no doubt added intentionally.

It has also been pointed out that the direct determination of iron in spiegeleisen is influenced by the unexpelled hydrocarbons (Riley, *Proc. Chem. Soc.*, vol. ii., 1877), an objection which will obviously apply to most of the iron alloys.

Small quantities of organic matter or copper do not interfere with the results obtained by the following method:—

A weighed portion of the alloy is dissolved in dilute

hydrochloric acid, a slight excess of potassic chlorate is now added, and the liquid well boiled to expel the chlorine compounds. By this treatment the small quantity of organic matter is decomposed, and the copper passes into the solution. The iron is now reduced by means of a solution of sodium sulphite, and after the excess of sulphurous acid has been expelled by boiling, the standard solution of bichromate is added in the usual manner.

Newburn Steel Works,
near Newcastle-on-Tyne.

THE SEPARATION OF COBALT AND NICKEL AFTER OXIDATION IN AN AMMONIACAL LIQUID.

By ADOLPHE CARNOT.

The problem of the separation of cobalt and nickel has been the subject of many researches. Among the methods proposed the author refers only to those which depend on the differences of the properties of the two metals when they have been submitted to peroxidation in an ammoniacal solution.

Such a process was proposed by M. Terreil (*Comptes Rendus*, lxii., p. 139, 1866). After boiling with permanganate in slight excess the solution is acidified with hydrochloric acid. On cooling a sparingly soluble purpureo-cobaltic chloride is deposited, but a portion of the cobalt escapes precipitation. The process is not available in analysis, but it may serve for the preparation of cobalt salts perfectly free from nickel.

M. Delvaux (*Comptes Rendus*, xcii., p. 723, 1876) also proposes to peroxidise with permanganate and to precipitate the nickel from the ammoniacal solution by caustic potassa. The bulk of the cobalt remains in solution, but an important quantity is found in the precipitate with the nickel and manganese oxides. Even after a second repetition it is too important to be neglected.

M. Vortmann (*Monatshefte für Chemie*, vol. iv., p. 1, 1883) takes as oxidising agent hypochlorite of soda, and heats the ammoniacal solution for some minutes to transform the cobalt salt into purpureo-cobaltic and luteo-cobaltic salts. After cooling and an addition of pure water he precipitates nickel monoxide with an excess of potassa. The ammonio-cobaltic salt gives the liquid a red colour if there is an appreciable quantity or yellow if there are merely traces. This method gives very distinct indications for qualitative research, but it has not apparently been used for quantitative separations.

The author has studied the effects of bromine and of oxygenated water upon cobalt salts in presence of ammoniacal salts, and sought if the use of the reagents could furnish an effective means of separating the two metals.

For the use of bromine the metallic solution must be cold and acid or contain ammonium chloride. There takes place a brisk escape of gaseous bubbles, and the solution turns to a rose colour if it contains cobalt alone, but violet if nickel also is present. A roseo-cobaltic salt is formed.

Oxygenated water may be added either before or after supersaturation with ammonia. In the cold it produces at first a brown colour, which in a few minutes turns to a purple-red or a rose according as there is more or less cobalt, but to a violet-rose if the proportion of nickel is considerable. In heat the same change takes place in a few moments. But it is in the cold that the colouration should be observed, for if the blue tint of nickel remains on heating that of cobalt diminishes much in intensity, and may even cease to become appreciable to the eye. These points constitute good qualitative characteristics for cobalt.

The ammoniacal solution may be heated and kept for some time at 100° without losing its limpidity, but ultimately it turns reddish brown and becomes turbid. The cobalt is in the state of a purpureo-cobaltic salt in the purple liquid, and it is converted into a luteo-cobaltic salt if the boiling is continued. The final decomposition gives rise to a deposit of cobalt sesquioxide, but this deposit is incomplete and contains nickel. Hence this process cannot be used for the separation of the two metals.

The addition of caustic potassa to the cold liquid determines the complete precipitation of the nickel as monoxide, provided there is a sufficient excess of potassa, depending on the quantities of ammonium chloride and of free ammonia. A pure solution of the purpureo-cobaltic salt gives no precipitate under the same conditions. In a mixture of the two salts there is produced a greenish deposit which we might believe composed exclusively of nickel, but when it is received on the filter it is easily seen to be of a darker green, and if treated with very dilute nitric acid it leaves a yellowish brown, and the solution is tinged of a yellowish rose or brownish by a little of the cobalt salt. If we dissolve the precipitate entirely and repeat the same operations we obtain a rose liquid and a green deposit which still contains a small quantity of cobalt. A third operation leaves merely an imponderable quantity of cobalt. We may therefore thus determine nickel in the precipitate by converting it into peroxide or sulphide in order to free it from alkalies. As for the cobalt, it is obtained entirely either by boiling the alkaline solution, which leaves a light brown deposit of cobalt sesquioxide, or by precipitating the black sulphide with a current of sulphuretted hydrogen or with ammonium sulphide.

The author has attempted in vain to obtain at once a precipitate of nickel free from cobalt, both by varying the state of combination of the latter metal, by effecting the peroxidation in heat, or by heating the ammoniacal solution for a longer or shorter time with hypochlorite, bromine, or oxygenated water. The best results have been obtained by leaving the solution for a few moments at 100°, cooling, adding much water, and then pouring in a solution of potassa. But they have never been quite satisfactory at the first precipitation, the operation having to be repeated twice more. Still the method may be recommended, because it has the great advantage of showing clearly the presence of the cobalt by the rose colouration of the liquid as long as any traces of it remain.

In the course of these researches the author has repeatedly observed that on dissolving in hydrochloric acid the precipitate produced by potassa and then treating the liquid with oxygenated water and ammonia there remained a slight brown precipitate, which, on further submission to the same treatment, turned to a rose. It seemed to present some novel reactions, and the author thought he had met with the new metal the discovery of which has been announced by MM. Krüss and Schmidt. On closer examination the precipitate was found composed of alumina with small quantities of iron, cobalt, and nickel.—*Comptes Rendus*, vol. cviii., p. 741.

LECTURE EXPERIMENTS WITH NITRIC ACID.*

By PETER T. AUSTEN.

Nitric acid, when in the state of a gas, makes an admirable subject for lecture experiments. A number of experiments with the liquid form are given in Heumann† and other books on experimental chemistry, but the following experiments with the gaseous form I have not been able to find described. A flask can be filled with nitric acid gas by placing in it some strong pure nitric acid and

* Communications from the Chemical Laboratory of Rutgers College. From the *American Chemical Journal*, March, 1889.

† "Anleitung zum Experimentiren," p. 125.

boiling. This operation, however, takes some little time and is not always satisfactory, as the flask at first becomes filled with a mist. The better plan is to pour into a quart flask having a neck wide enough to admit a deflagration spoon, some commercial concentrated sulphuric acid in sufficient amount to cover the bottom of the flask about half an inch, and add to it ten to twenty grms. of potassium nitrate. The potassium salt is better than the sodium salt, as it is less liable to contain nitrites, which will discolour the gas by the liberation of N_2O_3. The nitrate should be added in the form of crystals of about one-quarter of an inch in size. If added in a powdered condition, the mass cakes, and requires considerable shaking to disintegrate it. The coarser kind behaves admirably, and on heating the mixture the gas is liberated quickly and evenly.

The flask is hung free on a stand and a small naked flame applied. The nitric acid gas is liberated in large amounts, and expels the air at once. This operation should be done under a hood, although, by regulating the heat carefully, it is easily possible to fill the flask and yet not drive off enough gas to cause discomfort. If the filling is done under a hood, the flask and stand are placed, when needed, on a lecture-table; heat, sufficient to prevent the condensation of the gas, being kept under the flask. The sulphuric acid solution on the bottom of the flask is practically invisible, and does not in any way interfere with the experiments.

Nitric acid acts in all of these experiments, except the last, as an oxidising agent, viz:—

$$2HNO_3 = H_2O + N_2O_4 + O.$$

It will therefore serve as a source of oxygen, and its reduction will be indicated by the formation of the red N_2O_4. The strong colour of this gas makes some of the experiments very striking. In fact, several of them are worthy of performance in the regular lecture course. The temperature of the gas lies between 90°—100°. To get the full effect of the phenomena, the experiments should be performed in a partially darkened room, which, while permitting the details of the experiments to be observed, makes the combustions appear more brilliant.

Candle.—A lighted candle continues to burn, giving a brilliant flame surrounded by a large pale halo. The peroxide, N_2O_4, as in all of these experiments, forms at first in a large halo about the flame, and eventually fills the flask. As this phenomenon occurs in every case, it will not be mentioned again. Owing to the heat of the gas, the candle melts rapidly. The dropping wax soon sets up an action with the mixture of sulphuric and nitric acids on the bottom of the flask. The experiment should be stopped before this begins.

Wood.—An ignited splinter of wood (a splinter fastened to an iron wire is best) burns energetically. A spark bursts into flame as in oxygen.

Charcoal burns brilliantly. If bark-charcoal is used, the scintillations in the red gas produce an unusually fine effect.

Steel Watch-spring.—The spring should be not over 1½ m.m. wide, and should be detempered. By winding sulphur-string about the end, igniting and introducing quickly, the steel soon ignites and continues to burn brilliantly, but with an effect quite different from the combustion in oxygen. In this case it is well to put a layer of sand half an inch deep in the flask to prevent fracture of the bottom by the falling globules of fused iron.

Phosphorus burns with an intensely bright light as in oxygen. It soon volatilises and fills the flask with flame. Here again the tinging of the light by the red peroxide, N_2O_4, produces a peculiar effect.

Sodium takes fire without preliminary heating, and burns with an intense yellow light. A small piece and a deep spoon should be used so as to avoid any chance of the melted sodium falling into the sulphuric acid, as such an occurrence is dangerous.

Magnesium when ignited burns with its characteristic white light.

Copper, zinc, and antimony I have been unable to make burn.

Illuminating Gas.—A flame of gas, issuing from a bent-up glass tip, when inserted, continues to burn with a brilliant white centre surrounded by a large red halo. At first the flame becomes musical, degenerates into a series of rapid slight explosions, and is extinguished. The tone varies with the size of the flame. After a certain amount of peroxide, N_2O_4, is formed, the flame is not extinguished, and the musical tone also soon ceases.

Hydrogen sulphide burns with a bright yellow flame. The flask becomes filled with thick vapours—probably a cloud of chamber-crystals arising from the action of the sulphur dioxide and water (which result from the combustion of the hydrogen sulphide) on the nitrogen tetroxide.

Hydrogen burns with an intensely white flame resembling the flame of illuminating gas just described. It does not become musical.

Caoutchouc.—A piece of black rubber tube, introduced in a deflagration-spoon, soon fuses and evolves gas, which ignites and burns with a large flame having a bright core and a pale halo. It the caoutchouc is ignited in the air, it burns with a white smoky flame. When now introduced, the flame entirely loses its luminosity and becomes as described.

Turpentine boils violently and emits white fumes, which soon ignite with a gentle explosion and burn with a luminous flame.

Carbon disulphide does not ignite spontaneously, but when ignited and introduced it continues to burn energetically. It soon volatilises and fills the whole flask with flame.

Benzene does not ignite spontaneously, but when ignited and introduced it burns quietly with a white flame.

Ether evaporates and reduces the nitric acid gas to the tetroxide, N_2O_4. When ignited and introduced it soon volatilises and fills the flask with luminous flame.

Hydrochloric Acid Gas.—A stream of the gas issuing from a turned-up tip did not react, nor could the gas be ignited by applying a flame at the point of mixture between the gases. Heating the tube through which the hydrochloric acid was delivered also failed to effect a decomposition.

Hydrobromic acid gas could not be made to react, although a slight decomposition occurred.

Hydriodic acid gas could not be made to ignite. On passing it into the nitric acid gas, however, decomposition and liberation of iodine gas took place. It is a difficult matter to regulate the evolution of hydriodic acid, so that my failure may have been caused by the irregularity of the pressure. Hofmann* has shown that drops of hot fuming nitric acid falling through an atmosphere of hydriodic acid produce a large red flame and deposition of iodine crystals. I shall make another attempt to ignite the gas, using a different form of apparatus.

Ammonia.—This experiment requires a little skill, but is not difficult. Ammonia is evolved in a six-ounce flask by heating a mixture of ammonium chloride, slaked lime, and water. The flask is clamped to a stand and heated with a small flame. The stop-cock to this burner must be accessible without leaving the experiment, for by it is controlled the evolution of the ammonia gas. The success of the experiment depends on getting the right-sized jet of ammonia gas. The ammonia gas is led into the nitric acid gas by means of a glass jet, the tip of which turns up. This jet is connected with the evolution flask by a sufficiently long rubber tube. The orifice of the jet should not be less than one-eighth of an inch in diameter; a small jet rapidly clogs and closes. The jet-tube should be about sixteen inches long, so that the

* *Ber. der chem. Gesell.*, iii., 658.

rubber connection may not be attacked by the nitric acid gas issuing from the flask. The tube is grasped with a pair of tongs, and lowered into the mouth of the flask. As the gases mix, a dense cloud of ammonium nitrate is produced. As soon as the jet is on a level with the mouth of the flask, it should be ignited by means of a wax gaslighter, and at the same instant the jet is lowered into the centre of the flask. If the jet is of the right size and the pressure is neither too great nor too small, the ammonia will ignite easily and, on lowering into the flask, will continue to burn with a fine yellow flame. When once in position and burning evenly, the flame can be considerably enlarged by increasing the heat under the ammonia flask. The evolution must be regular, and to this end the flame under the ammonia flask should be protected against draughts.

The flame is a peculiar one, consisting of a yellow centre, then a greenish yellow envelope, and then a carmine-red envelope. As the colour of the peroxide, N_2O_4, gets deeper the flame becomes unusually handsome. The products of combustion are presumably oxides of nitrogen, perhaps free nitrogen, although I have not yet established this. It is a more striking experiment than the combustion of ammonia in a current of oxygen.

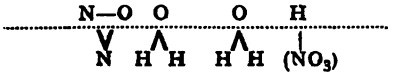
This experiment can be performed in a large oxygen globe. In this case the flask from which the ammonia is evolved must be provided with a trapped stand-tube filled with ammonia water to give a pressure. In this way, or by using a large jet and carefully manipulating a clamp on the rubber supply pipe, a large flame may be easily obtained.

Nitric Oxide.—A jet of nitric oxide, N_2O_2, introduced into nitric acid gas, reacts with it, the mixture turning at once red. The product of the reaction is probably nitrous acid,* $N_2O_2+2HNO_3=2HNO_2+N_2O_4$.

Nitrous Oxide.—A jet of moist nitrous oxide, prepared by heating ammonium nitrate, refuses to ignite in the nitric acid gas. I was surprised to observe, however, the formation of dense white clouds, which on examination proved to be ammonium nitrate. The reaction here is a synthesis of ammonium nitrate,—

$$N_2O+2H_2O+HNO_3=NH_4NO_3+HNO_3.$$

The molecule of nitric acid which appears on both sides of the equation is not an instance of chemical tautology, but is demanded since the rest, NO_3, that appears in the new molecule of NH_4NO_3 is not derived from the $2H_2O$ and the N_2O, but from the HNO_3; for water and nitrous oxide do not unite at a moderate heat. If I interpret the mechanism of this reaction correctly, it should be represented by the following diagram :—



THE CORROSION AND FOULING OF STEEL AND IRON SHIPS.†

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

(Concluded from p. 199).

One of the largest firms of composition manufacturers had enough curiosity to try the effect of zinc *versus* oxide of iron, and painted a patch of it upon a ship coated with his composition, and after a long voyage she returned with her protectives in perfectly good order, and had it not been for the patch containing zinc having had its position fixed by careful measurements, its whereabouts could not have been discovered. This is exactly what one would have expected; as long as the varnish remains intact oxide of iron, zinc, or, indeed, any substance which will not damage the varnish, does perfectly well; but had the vessel been allowed to continue until the varnishes had perished, then I venture to say that the patch containing the zinc would have shown better protection than those parts containing the oxide of iron. My ideas have undergone considerable modification during the past two years, but I still consider the views I put forward in my last paper were perfectly sound, and I am every day more and more convinced that the great object the composition maker has to aim at is the prolongation of the life and the effectiveness of the compositions, and not the multiplication of short-lived devices, however admirable in their action.

In the fifth class of protectives we have cement coatings; but these, together with such schemes as the covering the hull of the vessels with vitreous glazes, glass, &c., have of late years, as far as I know, entirely been abandoned. The action of cement on iron, however, must later on be discussed in its important bearing on the protection of the interior portions of the hull, for which it is largely employed, its weight and the difficulty of attachment rendering it unfitted for outside work.

In selecting a protective composition for the bottom of a vessel, one of the second or fourth class should be chosen, attention being given to the points I have indicated, which are that in the bituminous and asphaltic compositions all the original acids must be eliminated, and that in the varnishes of the fourth group quickly evaporating solvents should be avoided, and, if possible, zinc substituted for oxide of iron.

The vessel should have her plates as dry as possible during the application of the protective, and, if feasible, days on which the air is fairly dry should be chosen. The protective should not be too thick, as, if it is, it does not readily fill into inequalities in the plates; and, if in this way any air is enclosed, change of temperature will cause it to expand or contract, thus causing a blister to form, which will fill with sea water and set up rapid corrosion. The composition must either be elastic or else have the same rate of expansion and contraction as the iron; for, if not, the change of temperature will cause cracking and tearing of the composition, with disastrous results. The vessel, if she has to be scraped down to the bare metal, must be scrubbed free from all traces of rust, and where a well-adhering coating of composition exists, it should be painted over and not disturbed. In the case of a new ship, she must be pickled with dilute acid, to get rid of every trace of mill scale, and then washed down with some slightly alkaline liquid to neutralise every trace of acidity, the alkali in turn being removed by clean water. Under these conditions, and given a composition with good adhering properties, but little apprehension need be felt as to the ravages of corrosion on the metal of the ship's bottom, the chief risk being from abrasion and other mechanical injury to the composition, coupled with improper constituents in the anti-fouling compositions. The protection of the interior portion of the vessel, where the plates are exposed to the corroding action of bilge water, rendered more active by a high temperature, leakage from cargo, acids and sulphates from wet coals, and the presence of such electro-negative factors as coal-dust, scale, and rust, is a matter of quite as great importance as the exterior protection; whilst the great chance of mechanical abrasion during coaling and shifting of cargo, as well as the difficulty of getting at the lower portions of the hold to examine the condition of the plates, renders it a question of the gravest consideration. The corrosion found in the portions underneath the engine-seats, the bunkers, and the water-ballast chambers, especially near the engine-room, is often very serious, and needs most careful watching, which, from the position of these parts of the vessel, it is very hard to bestow upon it.

It must also be remembered that the bilge water in a

* Nitric oxide when led through concentrated nitric acid forms nitrous acid.—Gmelin-Kraut, 6 ed., i., 2 Aufl., 454.

† Read at the Thirtieth Session of the Institution of Naval Architects, April 12th, 1889. The Right Hon. the Earl of Ravensworth, President, in the Chair.

vessel is in constant motion, and that the air in these parts of the vessel may be expected to be exceptionally rich in carbonic acid gas, which, as I have before shown, is the most important factor in corrosion. Under these conditions any abraded portion would probably be continually washed over, and then exposed to the foul air, a condition of things most conducive to rapid rusting. There are three main classes of protectives for the interior of a ship—

1. Cements.
2. Bituminous coatings.
3. Paints.

The first of these, the cement coatings, have many good points to recommend them, but they also have many serious drawbacks.

The rigidity, firmness of adherence and endurance, are all of them points of the greatest importance, and there is no doubt but that the silicates present in the cement in time, not only bind the cement into a mass of wonderful hardness, but also bind the cement to the iron. A point to which I should like to draw your attention, however, is that a thin coating of Portland cement is highly porous, and that it can be permeated by liquids and gases. Suppose, now, that some copper scale from the interior fittings had fallen into the bottom of the vessel, and had been converted into soluble salts of copper by the saline bilge water, this solution would soak through the capillary orifices in the cement, until it came in contact with the iron below, when the copper would be deposited on the iron, and rapid galvanic action set up, the cement being loosened, and to a certain extent lifted, by the formation of rust, whilst corrosion would gradually extend under the cement, giving on the outside of the coating but little sign of the damage taking place below it.

Also the hardness and rigidity of the cement gives it a tendency to crack away from the metal when any strain is thrown on the plates, or during any expansion or contraction of the metal; whilst any repairs on the outside of the ship, such as making a boring to test the thickness of plate, replacement of rivets, &c., would undoubtedly cause a loosening of the cement coating within, and, wherever a loosening takes place, the space between the cement and the plate will quickly be found to become a starting-point for corrosion, which quickly spreads and loosens the cement, and will only be discovered by chance.

It is for this reason that I consider bituminous or asphaltic varnishes, freed from any trace of acid, and applied hot, or sound, tough paint, preferable to cement; as, although they are not so hard, yet if serious corrosion should be set up, it is easily discovered and stopped before much damage results, whilst, being impervious to moisture, deleterious solutions, either from the coal bunkers or cargo, would be prevented from acting upon the skin of the ship.

In approaching the subject of fouling, one is impressed with the apparent hopelessness of obtaining any reliable information from the successes or failures registered by the bottoms of the vessels in the Service, or in the Mercantile Marine. Hundreds of ships may be examined, and their condition and the nature of the compositions used upon them registered, and just as one begins to feel that the key to the mystery is within one's grasp, a whole series of results so abnormal suddenly comes to light that it seems impossible to reconcile them with one's previous experience. A ship may sail half a dozen times to the same waters, coated with the same composition—on four occasions she will come home clean, and in good condition, whilst on the other two voyages she may accumulate an amount of weed and animal life sufficient to knock down her speed from nine knots to five. Moreover, if the compositions with which she was coated be examined, and scrapings taken from her on her return, no cause will present itself that can in any way explain the great difference in her condition. After several years' close observation, however, certain factors begin to make themselves apparent. Ships at sea from March to August show a worse average than those afloat from August to March; one also begins to realise that the amount of fouling increases enormously if the ship has been long at anchor—ships which have been lying at the mouths of rivers, although quite clean in the brackish water, foul much more rapidly on going to sea than vessels which have been cruising, or even at anchor for the same time, in salt water; and, finally, certain ports and certain seas seem to exercise a deleterious effect, both as regards corrosion and fouling, which is not to be found elsewhere.

Turning back to the naval history of the past, we find that fouling is no new trouble born with the advent of our present iron monsters; but that it has been the one trouble that the combined engineering and scientific skill of many centuries has been unable to overcome.

With our wooden ships, metallic copper sheathing, if it were of the best kind, answered the purpose fairly well; but then the copper wasted so fast that inferior kinds and alloys were substituted to prevent the rapid loss, and, with the slowing down of the destruction of the copper, at once the trouble of fouling returned.

When iron ships began to replace the wooden ones, as was only natural, attempts were made to utilise the metal which had before given relief; but it was quickly found that the effect of the galvanic action set up by the copper was fatal to the iron plates of the ship, and attempts were then made to sheathe the ship with copper plates in such a way that they should be insulated from the iron of the vessel, a condition almost impossible to attain, and attended with great risk should any accidental injury to the insulation take place. Early in the history of iron shipbuilding the idea was started of using coatings of paint, so prepared as to fulfil the same functions as the copper plates had done; but from 1840, when the first paint of this kind was patented, down to the present day, when there are upwards of thirty-two different compositions in the market, very little progress has been made in their manufacture, and the best of the present compounds cannot be relied upon for keeping a ship's bottom even fairly free from fouling for periods extending beyond nine months, and I am personally convinced that the reason of this is to be found in the fact that a start was originally made in a wrong direction.

The idea which originally led to the present class of anti-fouling compositions was that the copper salts formed by the action of the sea-water on the metallic sheathing owed a considerable portion of their value as anti-foulers to the poisonous action they exerted upon marine animal and vegetable growths; but, when an observer comes to study the natural history of these lower forms of animal life and vegetation, it is gradually forced upon one that it is only in the early stages of their growth—the germ period—that metallic poisons can affect them. Seaweeds do not take in the constituents they require for their growth by means of their roots, as is, to a certain extent, the case with ordinary plants, but absorb them by means of their pores from the water itself, the root only serving to attach them to the solid they choose for their resting-place; and it is also well known that when once a marine plant which has passed the first stages of existence is dislodged or torn from its support, it cannot re-attach itself to anything else, whilst most of the mineral poisons have little or no effect upon their life and growth.

In the same way we find that, with the animal life found on a ship's bottom, the under side is used to cling on with only, and not as an extractor of nourishment, and that, therefore, after the seeds and germs have once obtained a foothold on the side of the vessel, no amount of poison which can be put into a composition will have any effect upon them. Metallic poisons undoubtedly do exert an influence upon the germs in their earliest stages; but after that they are perfectly useless as anti-foulers, and only imperil the plates of the vessel.

The germs of both kinds of growth are of necessity more abundant in the surface-water near shore than in

deep water, and, therefore, the period when the ship is in port is the time when the germs are most likely to make good their attachment, after which their further development is, unless other methods of getting rid of them are employed, merely a matter of time.

On examining the conditions under which a vessel is placed when coated with a composition which relies, for its anti-fouling powers, on metallic poisons only, we at once see the reasons which must make such a coating of little or no avail. In the composition we have drastic mineral poisons, probably salts of copper, mercury, or arsenic, which have been worked into a paint by admixture with varnishes of varying composition, and each particle of poison is protected from the action of the sea-water by being entirely coated by this vehicle; that this must be so is evident, or the composition would not have sufficient cohesive power to stick on the ship. As a rule, care is taken to select fairly good varnishes, which will resist the action of sea-water for, perhaps, two or three months, before they get sufficiently disintegrated to allow the sea-water to dissolve any of the poison; whilst, even with the accidental or intentional use of inferior varnishes, three or four weeks will pass before any solution can take place, and any poison be liberated to attack the germs. A ship is dry-docked, cleaned, and, her anti-fouling composition having been put on, she goes probably into the basin to take in cargo. Here she is at rest, and, with no skin friction or other disturbing causes to prevent it, a slimy deposit of dirt from the water takes place, and this, as a rule, is rich in the ova and germs of all kinds of growth, whilst the poisons in her coating are locked up in their restraining varnish, and are rendered inactive at the only period during which they could be of any use. After a more or less protracted period the ship puts to sea, and, the perishing of the varnish being aided by the friction of the water, the poisonous salts begin to dissolve or wash out of the composition; but the germs have already got a foothold, and with a vessel sweeping at a rate of, say 10 to 12 knots through the water, the amount of poison which can come in contact with their breathing and absorbing organs is evidently so infinitesimally minute that it would be impossible to imagine it having any effect whatever upon their growth. If the poison is soluble, it is at once washed away as it dissolves; if it is insoluble, then it is also washed away, but there is just a chance that a grain or two may become entangled in the organs of some of the forms of life, and cause them discomfort. As the surface varnish perishes, the impact of the water during the rapid passage of the vessel through the water quickly dissolves out or washes out the poisonous salts, and leaves a perished and porous, but still cohesive, coating of resinous matter, which forms an admirable lodgment for anything which can cling to it; and by the time the vessel lays-to in foreign waters, teeming with every kind of life, the poison, which would now again have been of some use, is probably all washed away, and a fresh crop of germs are acquired, to be developed on the homeward voyage, and a "bad ship" is reported by the person who looks after her docking. It is evident that a poison, even if it had the power of killing animal and vegetable life in all stages, could only act with the vessel at rest, unless it were of so actively corrosive a nature as to burn off the roots and attachments of the life rooted to it, and if it did this, what, may I ask, would become of the protective composition and the plates of the vessel? And I think it is also evident that any poison so used must be under conditions in which it is very unlikely to be in a position to act when it might do good.

The lamentable failure of composition after composition of this kind has gradually reduced them in number to some ten or twelve at the present time, and in most cases it is low price alone which keeps them in the market.

The practical proof, given by experience, that poisons alone are unable to secure a clean bottom soon led many inquirers to the conviction that it was the exfoliation in the case of copper which had acted in giving fairly good results, and in many compositions the attempt has been made to provide a coating which shall slowly wash off, and, by losing its original surface, shall at the same time clear away germs and partly developed growths, and so expose a continually renewed surface, in this way keeping the bottom of the vessel free from life. There is no doubt that when this is successfully done, a most valuable composition will result, but the practical difficulties which beset this class of anti-foulers must not be overlooked. In order to secure success the composition must waste at a fairly uniform rate, when the ship is at rest, and also when she is rushing through the water; and this is the more important in the case of service vessels, as in many cases they spend a large percentage of their existence at anchor, or in the basins of our big dockyards. If a composition is made to waste so rapidly that it will keep a vessel clean for months in a basin, then you have a good composition *for that purpose*; but send the vessel to sea, and under conditions where you have a higher temperature, and the enormous friction caused by her passage through the water exerting its influence upon the composition, and you will find that the coating, which did its work well for six months at rest in the basin, will, in the course of one month under these altered conditions, be all washed away, and fouling will be set up. Noting this result, the manufacturer renders his composition more insoluble—less wasting—and so obtains a coating which, when the vessel is in motion, scales just fast enough to prevent fouling, and good results at once follow; the composition is then put on the same or other vessels, and they take a spell of rest in the basin, and bereft of the aid of the higher temperatures, and the friction of the water, the composition ceases to waste fast enough, and bad results at once have to be recorded.

There is no doubt that this is the true explanation of the wide discrepancies which are found between the compositions in the Navy and in the Mercantile Marine—take any of the big lines, their steamers are running at a fairly uniform rate of speed, and the periods of inaction are as short as the desire not to waste the charge on the capital they represent can make them, and under these conditions, by varying the constituents in the varnishes used for anti-fouling purposes, it is fairly easy, given the necessary data, to so constitute a composition as to secure admirable results; but when you come to apply this same coating to an ironclad, running at various speeds, and as often at rest as in motion, then you at once find that the composition you before imagined to be all that could be desired fails just as lamentably as the tribe of anti-foulers which preceded it. It is not so very long ago that I had the honour to serve on an Admiralty Committee under the able guidance of Admiral Colomb, and after inspecting many vessels in the Mercantile Marine, and watching all the dockings of service vessels over a considerable space of time, we were forced to the conviction that it was only in very rare cases that the condition of the bottoms of Her Majesty's ships at all approached the freedom from fouling to be found in the ships belonging to the big companies, with the result that some of the most successful of the compositions in the Mercantile Marine were brought into use in the Navy, and I believe the reports of the dockings since they have been adopted will amply prove the existences of the difficulties I have mentioned.

Another factor which is often overlooked, and which tends to give misleading results, is the action of brackish water, which, in many cases, seems to exert a special action in keeping the bottom of a vessel clean, the fresh water having a tendency to disagree with certain forms of marine growth, whilst the salt water is apparently equally unpalatable to the fresh-water forms of fouling.

In most of the compositions now in use attempts are made to combine strongly poisonous substances with exfoliating and wasting coatings, and this is done by either using metallic soaps, the basis of which is, as a rule,

copper, or else by charging a perishable and easily washed off varnish with poisonous salts, consisting as usual of compounds of either copper, mercury, or arsenic, and in some cases all three.

As I have before pointed out, I do not think the presence of these substances exerts any deterrent action upon the fouling, save perhaps when the vessel is at rest; but they exert undoubtedly an important influence upon the rate of exfoliation, as when the perishing of the varnish exposes them they dissolve, or are washed out, and in this way tend to disintegrate and clear away the surface more rapidly, an important and decidedly useful function, but one which might be more cheaply performed by substances other than high-priced metallic poisons.

The use of metallic poisons of the character indicated throws an increased burden upon the protective composition, as, should the latter become abraded by friction of chain cables, barges alongside, or any other cause, the iron of the vessel will be attacked by the metallic salts, either present in the soluble form in the anti-fouling composition, or rendered so by the solvent action of the saline constituents of the sea-water, the action of the metallic salts being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way, but copper is by far the most objectionable, from the fact that the salts formed by the action of the sea-water upon the compounds used in the compositions are far more soluble than the corresponding salts of mercury, and are, therefore, liable to be present in much larger quantity, and so exert comparatively a much more injurious action on the plates.

As an illustration of this, two equal portions of sea-water were saturated, the one with copper chloride, the other with mercuric chloride, and into each a piece of steel, planed upon one side, and of about equal weight and size, was placed, and left for four days. At the end of this period the two plates were removed, and after being cleaned and dried were again weighed, when it was found that the one exposed to the copper saturated sea-water had lost 22·2 per cent in weight, while the plate exposed to the mercurial solution had only lost 3·6 per cent, this being due to the much larger amount of the copper salt soluble in the sea-water.

On now placing these plates in clean sea water, corrosion went on in each case with extreme rapidity, and after being exposed for a month they had both wasted to about the same extent, that is to say, when once deposited on the iron, mercury is practically as injurious as copper.

I am quite aware that this experiment is not at all likely to be carried out in practice, and none can have a greater conviction of the inutility of small laboratory experiments than I have, as they lack all the factors of mass of material and atmospheric influence which play so important a part in a question like the presence; but such an experiment gives one a definite and fairly correct idea of the relative rate of action of the two poisons upon the plates.

All the time the ship is in motion the wash of the sea-water will prevent the metallic poisons doing the plates or the marine growths much harm, but there is one phase of this question which I think has been overlooked. I need not point out that in certain ports there is a fashion in compositions, and that most of the homes of the Mercantile Marine have some pet local composition which is largely used at the particular port. If, now, many ships are laying in a basin, taking in and discharging cargo, and if the prevalent compositions contain copper, it is evident that a certain quantity will go into solution in the water, which often does not undergo frequent or rapid change, and under these conditions every ship in the basin will be exposed to the same danger, and wherever an abrasion has taken place in the protectives, there copper will be deposited on the iron, causing corrosion and destruction of the plates; and it must be remembered that when the vessel is next docked and coated no amount of scraping will remove the fine particles of copper deposited in the pitted and corroded portions of the plate, and so finely divided as to be invisible to the eye, but that it will remain and carry on its destructive work under the new coatings of protective.

It is, I think, a well-recognised fact that, when a vessel coated with a copper compound has become corroded from failure of her protective, or from abrasion, even an entire change of composition does little or no good in stemming the tide of corrosion, until after some considerable period has elapsed, a result which is due to the same cause; and, inasmuch as copper compositions are a source of danger, not only to the ships coated with them, but to any others which may be at rest in the same basin, I do strongly urge upon the manufacturers to abandon the use of these deleterious compounds, and to use others equally efficacious and free from the grave objections I have enumerated.

At the present time 15 out of the 32 principal compositions rely upon copper in some form or other as the basis of their anti-fouling composition, and in one which has enjoyed considerable favour finely divided metallic copper itself is used, and should a vessel coated with it, after the varnishes had commenced to disintegrate, be moored alongside an iron ship by a chain cable, or even by a wet hawser, a big galvanic couple would be formed at the expense of serious damage to any exposed iron.

In the history of anti-fouling many attempts have been made to obtain highly glazed and glass-like surfaces which it was hoped would withstand the action of sea water, and afford no lodgment to marine growths; but even glass itself is slowly acted upon by sea water, and, when once roughened on the surface, will foul, whilst the rigidity of such coatings, and the straining and cracking consequent on unequal expansion and contraction of the plates and their coating, offers a serious obstacle to any such scheme.

In concluding this long paper, I wish to point out that in the present phase of the anti-fouling question, and until some new principle for preventing marine growth has been advanced and successfully adopted, satisfactory results can only be insured by an intelligent use of the existing compositions.

The protective composition is the important composition, and care must be taken to obtain the best in the market, as, if the protection is good, the plates remain uninjured even if fouling take place. The anti-fouling composition to be used with it must either be elastic, or have the same rate of contraction and expansion as the protective, and must—at any rate in the Navy—be chosen to suit the work to be done, such as contain copper compounds being carefully rejected, whilst preference should be given to those which rely on exfoliation rather than mineral poisons. If a vessel is to remain at rest for a considerable period, an anti-fouling composition which exfoliates rapidly, and which also contains poisons known to act on germ life, must be used, the amount of such poison depending on the seasons and the waters in which the ship is to be; whilst if a vessel is to be continually running, then a slowly exfoliating composition must be employed, and a very small percentage of poison is all that is required, as skin friction and the comparative absence of the germs and spores in deep water will do the rest.

Our ships represent an enormous capital, and any trouble or care which will prolong their existence is well worth taking and will be amply repaid, and at the present time a heavily corroded and foul vessel means either ignorance or negligence on the part of those who have the responsibility of deciding on the composition to be used, and, finally, it must be clearly borne in mind that there is no anti-fouling composition which ever has been

made, or probably ever will be made, that will answer for all cases, and that until this is clearly recognised, the present unsatisfactory condition of the question will exist.

ON THE

BEHAVIOUR OF PHENOLPHTHALEIN WITH AMMONIA.

By J. H. LONG.

THE peculiar action of ammonia on phenolphthalein was first pointed out by Beckurts, I believe, in a paper in the *Pharmaceutische Centralhalle*.* Soon after the experiments of Luck† were published, showing the great value of this substance as an indicator, it came into general use in Germany, and was even incorporated among the tests of a new edition of the German Pharmacopœia then published. Schlickum, in his "Commentary on the German Pharmacopœia," 2nd Ed., states in one place that the behaviour of litmus and phenolphthalein in the titration of acids with ammonia water is the same, while in another place he remarks that the presence of ammonium salts interferes somewhat with the delicacy of the titration when phenolphthalein is the indicator. Beckurts shows the error into which a number of writers had fallen in this regard, by giving a series of tests carried out with different indicators. In the following year Flückiger‡ published experiments on the sensitiveness of phenolphthalein, leading to the conclusion that it could not be employed with ammoniacal solutions. In the excellent papers by Thomson,§ a similar conclusion is reached.

In the *Pharmacist*‖ I published the results of a long series of experiments on the action of phenolphthalein, and, among other points, I touched on the want of delicacy with ammonia. In that paper I offered an explanation of this behaviour, suggested in part by a remark of Baeyer¶ on the formation of phenol-di-imido-phthalein, and partially confirmed this explanation by a number of experiments. Since then I have again taken up the subject, repeating the old experiments and adding new ones, which I think afford a full confirmation of my former suggestion. It is this later work which I wish to present here in detail.

When a few drops of an alcoholic solution of phenolphthalein are added to a strong solution of soda, the deep red colour which forms at first vanishes in a short time—within a minute, if the soda is sufficiently strong. The colour can be restored by partial neutralisation with acids. When the indicator is added to strong ammonia solution (26 per cent), a red colour is produced which is more permanent, fading completely only after hours or days.

In this case, that is, after the *complete* disappearance of the colour, addition of acid produces no change. If the acid is added before the colour is fully discharged it becomes much brighter.

When phenolphthalein is added to a very weak soda solution, the red colour produced seems to be indefinitely permanent; but with weak ammonia it vanishes sooner or later, the interval between the mixing of the solutions and the disappearance of colour depending on several factors, as dilution, temperature, and strength of indicator.

There are, therefore, important differences between the action of soda and that of ammonia on phenolphthalein. If to a definite amount of a standard solution of hydrochloric acid containing a few drops of the indicator, standard ammonia solution be added, something more than the theoretical amount of the latter must be used to give the permanent red colour. However, by increasing the amount of indicator added, or by cooling the solutions, the colour can be obtained by nearly or quite the equivalent number of c.c. of ammonia.

A similar result is obtained by adding soda solution to a solution containing, along with free mineral acid, some salt of ammonium and the indicator. The effect of temperature was shown by the following experiments. I prepared half normal solutions of hydrochloric acid and sodium hydroxide and a solution of ammonium chloride containing 100 grms. in one litre. I took now 25 c.c. of the acid, 10 c.c. of the ammonium chloride, 65 c.c. of water, and a few drops of the indicator. To the mixture, slightly less than 25 c.c. of the sodium hydroxide was added, the whole was cooled to the desired temperature, and then more sodium hydroxide was run in to colouration. The results obtained at various temperatures are given in this Table:—

Temperature.	C.c. N/2NaOH.
6·5	26·2
13·5	27·0
22·5	27·6
30·0	28·1
38·0	28·7
49·5	29·9
62·0	31·0
69·1	32·0
76·0	32·8

The final reaction was in no case as sharp as in a titration between the alkali and acid alone, but the results are close approximations. Something similar is shown in the following experiments, which disclose likewise the effects of excess of ammonium chloride. Here I employed normal solutions of hydrochloric acid, sodium hydroxide, and ammonium chloride, and for each experiment took 25 c.c. of acid, a definite quantity of ammonium chloride, and added enough water to make 100 c.c. In each case 1 c.c. of a one-tenth per cent solution of phenolphthalein was added, and then caustic soda from a burette to colouration.

The solution in the beaker was kept at a temperature of 0° C., and that in the burette as near this as possible. The experiments were repeated for each mixture three times, and gave closely agreeing results, the end reactions being quite satisfactory and sharp. In the following table the mean of the results from the three tests is given:—

No	HCl. C.c.	NH_4Cl. C.c.	H_2O. C.c.	NaOH required. C.c.
1.	25	5	70	25·
2.	25	10	65	25·08
3.	25	15	60	25·20
4.	25	25	50	25·28
5.	25	30	45	25·37
6.	25	50	25	25·68

These experiments show clearly that with the temperature sufficiently low, the disturbing action of small amounts of ammonium salts is very slight. They show also at what rate the disturbance increases with increasing amounts of ammonium chloride.

At a temperature of 20° C. I obtained the following results, working with the same solutions:—

No.	HCl. C.c.	NH_4Cl. C.c.	H_2O. C.c.	NaOH required. C.c.
1.	25	5	70	25·22
2.	25	10	65	25·38
3.	25	15	60	25·61
4.	25	20	55	25·82
5.	25	25	50	25·98

We find here differences in the amount of alkali required, varying between 0·2 c.c. for the weakest solution to 1 c.c. for that containing 25 c.c. of ammonium chloride, which amounts to an error of 4 per cent. In all these

* 1883, p. 333.
† *Zischr. anal. Chem.*, 1877, 332.
‡ *Ber. d. chem. Ges.* xvii., 592. Ref.
§ CHEM. NEWS, xlvii., 125, 135, and 184.
‖ 1885, 43; also CHEM. NEWS, li., 160.
¶ *Ber. d. Chem. Ges.*, xi., 1297.

cases the error is so large that it could not be neglected in any kind of practical work. However, by employing a larger amount of indicator, the error can be almost entirely corrected, as shown by the following tests:—

I used here 25 c.c. of the acid and 5 c.c. of the ammonium chloride solution at a temperature of 20° C.

1. With 2 c.c. of indicator required 25·12 c.c. NaOH.
2. With 4 c.c. of indicator required 25·02 c.c. NaOH.
3. With 6 c.c. of indicator required 25·00 c.c. NaOH.

By using larger amounts of the indicator, the final reaction is obtained with satisfactory sharpness.

In another series of experiments, ammonia was run into the solution containing hydrochloric acid and different amounts of the phenolphthalein. Where but a few drops of this were taken, the end reaction could not be observed accurately; with larger amounts the reaction was sharper, but only came after addition of an excess of alkali.

1. With 25 c.c. of acid and 5 c.c. of indicator I used 25·57 c.c. of NH_4OH.
2. With 25 c.c. of acid and 10 c.c. of indicator I used 25·28 c.c. of NH_4OH.

In presence of alcohol the reaction was always less distinct than with water, and more alkali was required to bring it.

The above results seem to indicate that ammonia combines with phenolphthalein, forming, to some extent, a colourless compound, besides forming a coloured one as does sodium hydrate; and also that this colourless body is produced more quickly as the temperature is higher or the ammonia stronger.

I expressed the opinion in my former paper, referred to above, that the phenol-di-imido-phthalein discovered by Baeyer is the compound formed here, and that this explains the peculiar reaction.

The experiments given below seem to confirm fully this view. Baeyer* states that phenolphthalein and aqueous ammonia heated to 160°—170° in sealed tubes for some hours react on each other in this way:—

$$C_{20}H_{14}O_4 + 2NH_3 = C_{20}H_{16}N_2O_2 + 2H_2O.$$

The phenol-di-imido-phthalein is a colourless body soluble in alkalies without colour, but which dissolves at a high temperature in acids, with formation of an ammonium salt and phenolphthalein:—

$$C_{20}H_{16}N_2O_2 + 2H_2O + 2HCl = C_{20}H_{14}O_4 + 2NH_4Cl.$$

I prepared the product by the following methods:—

1. Three grms. of phenolphthalein and 30 c.c. of strong ammonia were heated during three hours in a sealed tube to 160° C. The tube was then opened and the contents neutralised with hydrochloric acid. This precipitated a gummy mass, which was washed thoroughly with water, and finally dissolved in 90 per cent alcohol. The solution, after filtration through bone charcoal, was evaporated to dryness. The residue left was dissolved in a mixture of equal parts of benzene and alcohol. The solution was allowed to evaporate spontaneously, leaving a residue, which was heated to 120° C. to completely remove all traces of the solvent. The product then remained as a colourless mass of fine needle-shaped crystals.

2. Ten grms. of phenolphthalein were treated with 200 c.c. of strong ammonia solution in a flask kept hot on a water-bath during fifteen hours; at the end of that time the solution was neutralised with hydrochloric acid, and an insoluble gummy mass formed was treated as under 1.

3. Ten grms. of phenolphthalein were dissolved in 200 c.c. of strong ammonia water (26 per cent) at the ordinary temperature of the room. The colour formed at first disappeared in four days without application of heat. I then neutralised with hydrochloric acid, and obtained the same product as above, which was treated in the same manner.

The three substances so obtained appeared quite similar, and turned red when moderately heated in a porcelain dish, melting finally at a higher temperature. They dissolved in sodium hydroxide solution without colour. When heated to 110° C. with hydrochloric acid they formed ammonium chloride and phenolphthalein, as shown by various tests. They all dissolved in strong nitric acid with a marked yellow colour, which disappeared on addition of alkali.

It is apparent, therefore, that the phenol-di-imido-phthalein can be formed at ordinary temperature as well as in a sealed tube at 160°, although the preparation of a large amount at the lower temperature would require a much longer time.

The combination between the free alkali and the trace used as indicator in a practical titration would naturally require but a very short time at the ordinary temperature.

The rapidity of liberation of ammonia from an ammonium salt by fixed alkali depends on the temperature, and hence the very slight disturbance of the reaction with the mixed solutions in the above experiments carried out at a low temperature. Addition of sodium hydroxide seems to aid the reaction with ammonia solution, as shown by experiments in which I added the phenolphthalein to ammonia solution and then the sodium hydroxide from a burette. With half-normal solutions the colour was lost in half an hour by mixing 25 c.c. sodium hydroxide, 20 c.c. ammonia, and 0·2 c.c. of the indicator. Similar results were obtained with other solutions.

The above experiments show that the phenolphthalein can be used with ammonia by taking certain precautions, and they also suggest why the behaviour of this alkali was not sooner recognised. By working at a low temperature with a sufficiently large amount of the indicator, it was shown that fairly sharp results can be obtained. However, as we have other good indicators, it may never seem necessary to take these precautions.

After the introduction of the phenolphthalein as an indicator, some time elapsed before its extreme sensitiveness was realised, and undoubtedly more was then added to a solution than is now considered necessary. Under these circumstances the difference in behaviour between soda and ammonia would scarcely be noticed, and it remained for later observers, working with less of the reagent, to detect the discrepancy.

I am greatly indebted to my assistant, Mr. Mark Powers, for help in the details of the above experiments.—*American Chemical Journal*, vol. xi., No. 2.

* *Ber. d. chem. Gesell.*, xi., 1297.

ON THE

CONVERSION OF SOME OF THE HOMOLOGUES OF BENZOL-PHENOL INTO PRIMARY AND SECONDARY AMINES.*

By RACHEL LLOYD.

(Concluded from p. 196).

CARVACROL.

FROM the results obtained with thymol it was natural to suppose that its isomer, carvacrol, would yield similar products.

The carvacrol used was obtained from Schuchardt, and boiled constantly at 236°. The same proportions of zinc-ammonium bromide and ammonium bromide were used as in the foregoing investigations, and the mixture was heated for the same number of hours at 350°—360°.

The reaction-mass consisted of a light golden-brown under-layer, and a darker overlying layer of a granular consistence, intermixed with a considerable quantity of a light yellow oil. The sides of the tubes were covered with drops of water. Pressure, almost none.

* "University Studies, Published by the University of Nebraska," October, 1888.

In the corresponding experiments with carvacrol, zinc-ammonium chloride, and ammonium chloride, the pressure in tubes was considerable; the escaping gas possessed an agreeable aromatic odour and burned with a feeble flame. In these experiments more carbonised substance was formed than when the bromine compounds were employed. The products were isolated by previously described methods.

Carvacrylamine:—

$$N\begin{cases}C_{10}H_{13}\\H\\H\end{cases} = C_{10}H_{13}NH_2,$$

a yellowish brown oil distilled by the first distillation at 240°—245°, leaving a small quantity of carbonised substance in the bulb; by the second, almost entirely between 241°—242°. The freshly distilled amine was nearly colourless, and upon exposure to the air turned yellow, then brown. It solidified and crystallised indistinctly at −16° C.

The analysis gave the following result:—

0·1497 grm. substance gave 0·4448 grm. carbon dioxide and 0·1351 grm. water, corresponding to 0·1213 grm. C. and 0·1501 grm. H.

Calculated for $C_{20}H_{27}N$.			Found.
C_{10}	120	80·54 per cent	81·03 per cent
H_{15}	15	10·06 „	10·02 „
N	14	9·40 „	— „
	163	100·00 per cent	

Dicarvacrylamine:—

$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\H\end{cases} = C_{20}H_{26}NH.$$

The raw, dark coloured, oily, secondary amine was distilled with super-heated steam; the oil which came over in light golden drops and floated on the surface of the milky distillate was extracted with ether, dried over caustic potash, and finally re-distilled in vacuum. The greater portion distilled at 344°—348°; above this temperature decomposition took place. The fraction so distilling was almost colourless, had a most pleasant odour, dissolved readily in alcohol, ether, and benzol. At −18° C. the body retained the consistence of an oil. With concentrated sulphuric acid, a golden tint was produced, which changed by the addition of a nitrate or nitrite first to green-blue, then to blue.

The analysis gave the following result:—

I. 0·1856 grm. substance gave 0·5814 grm. carbon dioxide and 0·1619 grm. water, corresponding to 0·15856 grm. C. and 0·01798 grm. H.

II. 0·2322 grm. substance gave 10·5 c.c. of moist nitrogen (thermometer 22° C., barometer 720 m.m.), equal to 0·011396 grm. N.

Calculated for $C_{20}H_{27}N$.			Found.
C_{20}	240	85·41 per cent	85·45 per cent
H_{27}	27	9·61 „	9·68 „
N	14	4·98 „	4·90 „
	281	100·00 per cent.	

The percentages of carbonised substance, unchanged phenol as well as the bases obtained by corresponding experiments with the bromides and chlorides of zinc and ammonium, are here tabulated.

Carvacrol.	Zinc-ammonium bromide. I.	II.	III.	Zinc-ammonium chloride. I.	II.	III.	
Carvacrylamine ..	30	35	36	28	27	25·6	p.c.
Dicarvacrylamine ..	40	38	39	32·1	29·6	27·4	„
Unchanged phenol ..	24·2	20	20·3	32	34·3	40·2	„
Carbonised substance	0·5	0·9	1	3	4·1	4·5	„

Derivatives of Carvacrylamine.

The platinum double salt—$(C_{10}H_{13}NH_2.HCl)_2PtCl_4$—was made by precipitating a hydrochloric acid solution of the amine with platinum chloride. A yellow precipitate in the form of needles shot out at once from the golden-coloured solution. These needles were re-crystallised from alcohol in beautiful prisms grouped in clusters. The crystals were dissolved with difficulty in hot water, but readily in hot alcohol and benzol.

An analysis of the salt dried at 100°—110° gave the following result:—

0·5024 grm. substance gave 0·1384 grm. platinum.

Calculated for $(C_{10}H_{13}NH_2.HCl)_2PtCl_4$.	Found
27·48 per cent Pt.	.. 27·55 per cent Pt.

Acetylcarvacrylamine:—

$$N\begin{cases}C_{10}H_{13}\\C_2H_3O\\H\end{cases} = C_{12}H_{17}NO$$

was formed readily by the action of acetic anhydride upon a calculated amount of the base. Action began at once, the solution became quite brown in colour. To insure complete reaction, the substances were warmed for an hour at 130°.

The white mass which separated was crystallised from a mixture of alcohol and water in glistening white plates, melting at 115°. The crystals dissolved in an abundance of hot water, more readily in benzol than in ether, with readiness in hot alcohol.

Benzoylcarvacrylamine:—

$$N\begin{cases}C_{10}H_{13}\\C_7H_5O\\H\end{cases} = C_{17}H_{19}NO.$$

To form this compound a grm. of the base was treated with an excess of benzoyl chloride. Action took place immediately with evolution of hydrochloric acid. Upon warming, a further evolution of gas took place, and a crystalline mass of a yellowish tint was formed. Upon treating the mass with sodium carbonate it became white and was crystallised from hot benzol in shining crystals.

The crystals had the appearance of flat rhombs and feathery aggregates, were insoluble in hot water, with difficulty soluble in cold, easily in hot alcohol, but readily soluble in ether or benzol; melting-point 102°.

The analysis gave the following result:—

0·2184 grm. substance gave 0·6455 grm. carbon dioxide and 0·1500 grm. water, equal to 0·1760 grm. C. and 0·1666 grm. H.

Calculated for $C_{17}H_{19}NO$.			Found.
C_{17}	294	80·63 per cent . ..	80·58 per cent
H_{19}	19	7·51 „ . ..	7·63 „
N	14	5·53 „ . ..	— „
O	16	6·33 „ . ..	— „
	253	100·00 per cent	

Derivatives of Dicarvacrylamine.

The platinum double salt—$(C_{20}H_{26}NH.HCl)_2PtCl_4$—was prepared after the method used with the double salt of dithymylamine. The product so obtained was more crystalline than the isomeric salt, and after thorough washing and drying over sulphuric acid in vacuum, granular feathery aggregates of a beautiful golden colour were formed.

The analysis of the salt dried at 100° gave the following result:—

0·2039 grm. substance gave 0·0464 grm. platinum.

Calculated for $(C_{20}H_{26}NH.HCl)_2PtCl_4$.	Found.
20·01 per cent Pt.	.. 19·93 per cent Pt.

The *hydrochloric acid salt*—$C_{20}H_{26}NH.HCl$—formed most readily by conducting dry hydrochloric acid gas into

a solution of the base in benzol. The salt was precipitated as a white granular crystalline mass, which was easily decomposed by water with separation of the base. The mass was filtered off, washed with benzol, and dried over sulphuric acid in vacuum. An analysis of the salt dried at 100° gave the following result:—

0·2464 grm. substance gave 0·1110 grm. silver chloride.

Calculated for $C_{22}H_{29}NH.HCl$.	Found.
11·18 per cent Cl	11·15 per cent Cl.

Acetyldicarvacrylamine:—

$$N\begin{cases}C_{10}H_{13}\\C_{10}H_{13}\\C_2H_3O\end{cases} = C_{22}H_{29}NO.$$

The method used in the preparation of this body was the same as that used with the isomeric phenols. The glistening white scales obtained by crystallising the product of the reaction in hot benzol were easily soluble in hot alcohol and in hot ligroin: melting-point, 78°.

The combustion gave the following result:—

0·2171 grm. substance gave 0·6480 grm. carbon dioxide and 0·1787 grm. water, corresponding to 0·1767 grm. C. and 0·0198 grm. H.

Calculated for $C_{22}H_{29}NO$.			Found.
C_{22} — 264 —	81·73 per cent	..	81·38 per cent
H_{29} — 29 —	8·98 ,,	..	9·12 ,,
N — 14 —	4·34 ,,	..	— ,,
O — 16 —	4·95 ,,	..	— ,,
323 —	100·00 per cent		

Summary of Results.

The above experiments have shown that primary and secondary amine, together with carbonised substance, are produced when isobutylphenol, isoamylphenol, thymol, and carvacrol are heated to 320°—360° with an excess of zinc-ammonium bromide and ammonium bromide, or with the chlorides of zinc and ammonium.

Better results were obtained by using the bromine compounds.

The percentage of amines reached its maximum—seventy per cent—with carvacrol; the three other phenols yielding only forty-five to sixty per cent of the original substance.

In a manner similar to that used with the cresols and xylenols, these more complicated homologues of benzolphenol have been converted into amines; but the bases so obtained have not formed chemical combinations so readily as the bases obtained from the phenols of simpler form.

So far as I know, the primary base—carvacrylamine—has not been previously described.* When freshly distilled, it is an almost colourless oil of a disagreeable odour; boiling-point, 241°—242°. In a freezing mixture it became solid with an indistinctly crystalline structure. Its derivatives are beautifully crystalline. For further identification of the amine, its platinochloride and acetyl and benzoyl derivatives were studied.

The secondary bases, namely, diphenisobutylamine, diphenisamylamine, dithymylamine, and dicarvacrylamine, are oily liquids which boil above 300°, are nearly colourless when first distilled, but colour on exposure to the air. The dicarvacryl and dithymyl bases have a most agreeable odour. In order to study more closely the character of these secondary amines, the platinum double salt and the acetyl and benzoyl compounds were prepared. With the exception of the platinochloride of dithymylamine, the products were well crystallised.

A summary of the work would be incomplete without mentioning the fact that efforts to obtain picrates of diphenisamylamine and dithymylamine were unsuccessful. An analysis of the products obtained by the action of an alcoholic solution of picric acid upon an alcoholic solution of the afore-mentioned bases, corresponded quite closely with the theory for picric acid. In crystal form and melting-point the substances exhibited marked differences. The products will be further examined with the hope of determining what molecular arrangement took place.

* Since these investigations were made, Söderbaum and Widman have obtained cymidin (carvacrylamine) by another method. See *Berichte der Deutschen chem. Gesellschaft*, xxi., 2127.

NOTICES OF BOOKS.

A Treatise on Chemistry. By Sir H. E. Roscoe, F.R.S., and C. Schorlemmer, F.R.S. Vol. III.—*The Chemistry of the Hydrocarbons and their Derivatives, or Organic Chemistry*, Part 5. London: Macmillan and Co.

This work, when complete, will be without doubt the foremost systematic treatise on chemistry which has ever issued from the British press. Other works, such as that of W. A. Miller, however useful, appear in comparison almost as hand-books—using the term in its English sense—and "Watts' Dictionary of Chemistry" from its form does not take up exactly the same ground. Another advantage of the work before us is that it embodies the results of the latest research, a point which in a rapidly-extending science like chemistry is of no small moment. The volume embraces the description of the benzene-hydrocarbons containing eight or more atoms of carbon, and it concludes with the terpenes and the camphors.

The authors discuss the groups styrolene, cumene, carbostyril, phenylpropiolic, cymene, laurene, mellitene; and proceeding to the compounds containing more than twelve atoms of carbon, the terpenes, and camphors, pinene, camphene, limonene, dipentene, sylvestrene, terpinolene, terebenene, and phillandrene groups.

Among the polyterpenes we find mention of caoutchouc, balata, and gutta-percha.

It is almost a superfluous task to say that the account given of all the many substances here described is correct, according to the present state of knowledge, and as complete as space will allow.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 14, April 8, 1889.

Fixation of Nitrogen by Vegetable Soil, with or without the Co-operation of Leguminous Plants.—M. Berthelot.—The author has succeeded in establishing by certain proofs that a fixation of atmospheric nitrogen really takes place principally in certain vegetable soils, giving rise to the formation of complex organic compounds of the order of the albumenoids, whilst it does not take place in the same soils if sterilised. These phenomena along with others tend to refer the fixation of nitrogen to the microbia contained in the soil. The fixation of nitrogen does not take place exclusively by means of the lower plants properly speaking, moulds, fungi, algæ, &c., which may be developed on the surface of the soil. On the contrary, the surface layer is often less rich in nitrogen than the entire mass. The question whether plants contribute by their aërial portion to the fixation of nitrogen requires a renewed study. It seems to the author difficult to contest in principle that such an immediate fixation takes place to a certain extent under

the continuous action of atmospheric electricity of feeble tension.

Experiments on the Putrefaction and on the Formation of Farmyard Manure.—J. Reiset.—The author commenced his researches in 1854 with the preconceived notion that nitrogen was gradually fixed during the slow combustion of organic matter in presence of alkaline carbonates. In 1856 he came to an opposite conclusion, viz., that in all cases when a nitrogenous organic matter undergoes putrid decomposition a part of its nitrogen escapes in the gaseous condition—a conclusion confirmed by the researches of Messrs. Lawes, Gilbert, and Pugh. The author considers, however, that the discovery of the chemical activity of microbia opens a new phase of this question. He mentions a *Bacillus denitrificans*, observed by MM. Gayon and Dupetit, which even decomposes potassium nitrate with an escape of pure nitrogen. He asks if there is not an abundant source of nitrogen during the decomposition of organic matter under water, and quotes an analysis made by Bunsen of the gases obtained from the mud of a pond in the Botanical Garden of Narburg. This gas, after removal of the carbonic acid, contained 51·5 per cent of free nitrogen.

Speed of Transformation of Metaphosphoric Acid.—Paul Sabatier.—At one and the same temperature the solutions are transformed the more rapidly in proportion as they are more concentrated. It is also accelerated with a rise of temperature.

Separation of Cobalt and Nickel after Oxidation in Ammonical Solutions.—Adolphe Carnot.—(See p. 208).

The Solubility of Salts.—H. W. Bakhurs Roozeboom.—A reply to M. Le Chatelier's memoir, inserted in *Comptes Rendus* for March 18, 1889.

Preparation of the Hydrochloric Ethers by Means of Alcohols saturated with Hydrochloric Acid and Heated in Closed Vessels with a Large Proportion of the Strongest Hydrochloric Acid.—H. Malbot.—The preparation of hydrochloric ethers by previous saturation of the alcohol with hydrochloric acid gas has not been found to give satisfactory results. The absolute quantity of water present is of less importance than the relative proportion of water and acid. A much better result has been obtained by first saturating the acid perfectly with hydrochloric acid gas and then adding a strong dose of the most concentrated hydrochloric acid.

On Methyl-acetanilide.—H. Girard.—The substance described by Dr. Dujardin-Beaumetz in the *Comptes Rendus* for March 18 is prepared by M. Brigonnet under the name exalgine. The substance, it is stated in the memoir, has the scientific name "ortho-methyl-acetanilide," and it is said that "like all the aromatic compounds, it may exist in three modifications, ortho, para, and meta." Now the name ortho-methyl-acetanilide is applicable only to a body described by Beilstein and Kuhlberg under the name *aceto ortho-toluide*, prepared by means of orthotoluidine and acetic acid. The substance prepared by M. Brigonnet is not novel; it was described by Hofmann in 1874. Its true name is methyl-acetanilide, and it cannot exist in three modifications, since the phenyl radicle contained in its molecule is not substituted.

Analysis of Cinchonas, and the Relative Solubility of their Proximate Principles in Water, Alcohol, and Dilute Hydrochloric Acid.—E. Landrin.—This paper will be inserted in full.

Solubility of Different Minerals in Sea-Water.—J. Thoulet.—The author has examined the solubility in sea-water of obsidian, pumice, amphibole, orthose, marble, shells (*Pectunculus philosus* and *Cardum edule*), and coral of the species *Cladocera*. The minerals were powdered, separated by sifting into uniform granules of the size of a small millet seed, dried in the stove at 125°, and separated into two approximately equal portions, each of which was carefully weighed. One set of the samples were placed in stoppered bottles with known volumes of filtered sea-water, agitating several times daily. After a week the water was drawn off by means of a filter-syphon, so that no solid fragment might be removed, and replaced by a new quantity of sea-water. The experiment lasted for seven weeks. The check portions were treated in a similar manner with distilled water. The solubility in sea-water was found extremely slight and notably inferior to the solubility in fresh water. This fact is explained by the total absence of free carbonic acid in sea-water, which has an alkaline reaction with litmus and coralline. In the cases of marble, orthose, shells, and coral the loss was negative on account of the algæ which germinated in the sea-water. The author therefore proposes to repeat the experiment in the absence of light.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Naphtha.—Will some reader kindly inform me how I can by calculation convert pounds of coal-tar naphtha into gallons? Also how I can by calculation reduce the percentage of coal-tar naphtha? For instance, supposing I have 100 gallons 50/90 benzol, testing 33 per cent 100° C., how can I reduce this to 50 per cent at 100° C. by calculation.—E. J. B.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.
—— Society of Chemical Industry, 8. "On Explosives," by C. Napier Hake.
—— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 7th.—Royal Institution, 3. "The Italian Renaissance Painters; their Education," by Jean Paul Richter.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 8th.—Geological, 8.
—— Society of Arts, 8. "Origin and Manufacture of Playing Cards," by George Clulow.
—— Microscopical, 8.
THURSDAY, 9th.—Royal, 4.30.
—— Royal Institution, 3. "The Science of Locomotion in its relation to Design in Art (illustrated by the Zoopraxiscope," by Eadweard Muybridge.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
FRIDAY, 10th.—Royal Institution, 9. "Optical Properties of Ozone and Oxygen," by Prof. Dewar, F.R.S.
—— Astronomical, 8.
—— Quekett Club, 8.
SATURDAY, 11th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.
—— Physical, 3. "On an Electrostatic Field produced by Varying Magnetic Induction," and on the Concentration of Electro-magnetic Waves by Large Cylindrical Lenses," by Prof. O. J. Lodge, F.R.S.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1537.

RESEARCHES ON THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C., Professor of Chemistry and Hygiene, R.C.S.I.;

and JOHN MACALLAN, F.I.C., Demonstrator of Chemistry, R.C.S.I.

Although selenic acid was prepared by Mitscherlich so far back as the year 1827, few chemists appear to have studied its properties. This want of interest in selenic acid is rather surprising, seeing that it possesses so close a relationship to sulphuric acid, which is so important a compound. Finding the chemistry of selenic acid so meagre, we resolved to make an investigation of this body, with the view of bringing, so far as we could, its chemistry abreast with that of sulphuric acid, and also in the hope that its study would yield results which might throw additional light on the relations of the latter acid. The following pages contain the results at which we have arrived.

Preparation of Anhydrous Selenic Acid, H_2SeO_4.

Selenic acid has hitherto been known only in a dilute form. When heated to upwards of 260° C. it commences to decompose into selenium dioxide, oxygen, and water, which prevents any further concentration. Berzelius describes it as containing, when of greatest strength, 4 per cent of water; but it has been obtained since his time, in a more concentrated condition, by Fabian, who, by evaporating the acid to a temperature of 265°, found it to have a strength of 94·9 per cent, and by placing this acid, while still hot, under the receiver of an air-pump, increased its strength to 97·4 per cent. Sulphuric acid, as is well known, has not been obtained in a perfectly anhydrous state by ebullition—although in its case decomposition does not occur; for when it reaches a strength of about 98·66 per cent it boils without further change. When, however, an acid of this strength is surrounded with a freezing-mixture, the anhydrous acid, H_2SO_4, crystallises out. An attempt was first made to obtain anhydrous selenic acid by similar means. Great care was taken to obtain an acid of pure quality. An examination was specially made for nitric, sulphuric, hydrochloric, and hydrobromic acids. Selenious acid, when present, was removed by diluting with about 30 parts of water, saturating with hydrogen sulphide in the cold, filtering, and concentrating on the water-bath. The acid thus treated was then examined for sulphuric acid and found to contain none. A portion of the acid, when ignited, left a residue equivalent to 0·07 per cent of the anhydrous acid present in the specimen used in the experiment; this was ascertained to consist of neutral sodium selenate, and was, of course, derived from an acid salt, of which it was necessary to take account in the succeeding experiments.

Some of this acid was gradually heated until the temperature rose to 250°. It was next poured into an open dish, and allowed to cool slowly over sulphuric acid, under an exhausted receiver. The strength was then taken with semi-normal soda solution, which was specially prepared for these experiments by making a solution in water of pure caustic hydrate prepared from sodium, and bringing it carefully to the required strength; 11·81 c.c. of soda solution were required for neutralisation by 0·4371 grm. of acid, equivalent to 97·75 per cent of selenic acid, being thus a little stronger than that obtained by Fabian in a similar way.

The acid thus concentrated was then poured into a stout wide glass tube, having one end closed, and the open end fitted with an indiarubber cork, through which passed a glass rod for the purpose of keeping the viscous liquid stirred, and a capillary tube for admission of air, in order to expose the acid to the full atmospheric pressure. The necessity for these precautions in the case of sulphuric acid has already been fully pointed out by Marignac (*Annales de Chimie et Physique*, xxxix. (1853), 184), the discordant results arrived at by various observers being probably due to the different conditions under which they worked. The latter precaution is particularly necessary, as we have observed that sulphuric acid occupies less volume in the solid than in the liquid state.

The temperature of the acid was then gradually lowered. Its viscosity increased as it became colder, until at a temperature of −51·5° C. it was as thick as soft pitch—the tube might be inverted without the acid flowing, and a glass rod could be moved in it only with great difficulty. Still it did not freeze, until, after vigorous stirring maintained for a couple of minutes, a crystal appeared, and then the entire mass almost instantaneously crystallised, the temperature rapidly rising. When removed to a warm room the crystals were rather permanent, and when nearly melted re-crystallisation could easily be induced by exposure to moderate cold as long as any crystal remained, showing that previous to freezing the acid had been in a more or less superfused condition. It was found to be impossible, however, to separate the crystals by draining the liquid portion, as the latter was so viscous that it carried the crystals with it. Under the microscope they were seen to be long prisms.

An attempt was next made to examine the conditions under which selenic acid becomes strengthened in a vacuum, with the object of obtaining, if possible, a more concentrated acid; and the following arrangement was made for the purpose:—The glass receiver of an air-pump was fitted tightly at its neck with an indiarubber cork, through which passed a bent tube, connected horizontally with another and wider tube containing solid potash. This was connected with a wide U-tube, filled with pieces of potash about half an inch long, and kept cool by immersion in a beaker of water. Connection was then made with a small stout flask containing the selenic acid, and varying in size from 100 to 250 c.c., as required. The potash tube next the receiver was intended for the purpose of preventing acid fumes from injuring the air-pump, and for the same reason a vessel of potash was placed within the receiver. The air-pump employed gave a very good vacuum; when all the connections were made and the pump exhausted there was often scarcely any appreciable difference in the levels of the columns of mercury in the gauge. For temperatures up to 100° the flask containing the acid was heated in a beaker of water; for higher temperatures oil was used. Soon after commencing the experiments it was found necessary to make an arrangement for the purpose of stirring up the viscous acid and exposing fresh surfaces to the vacuum, and the following plan was devised:—A test-tube, which fitted easily the neck of the flask, was shortened by removing evenly a portion of the open end. It was then inverted and pushed down into the flask, so that when the open end was below the surface of the acid the closed end extended sufficiently far into the neck of the flask to prevent the tube from being thrown down by the ebullition of the liquid. The vapour given off from the acid within the tube became gradually expanded as the temperature rose, and passed in a stream of bubbles through the acid, keeping it well agitated. The tube also served the purpose of preventing splashing from the boiling acid up into the neck of the small flask.

Some selenic acid, which had been previously partially concentrated, was kept in an open dish on the water-bath

* A Paper read before the Royal Society, May 2, 1889.

for four hours and its strength then determined: 0·6364 grm. required for neutralisation 14·72 c.c. of seminormal soda solution, equivalent to 83·68 per cent of selenic acid —a strength intermediate between a monohydrate and a dihydrate. The acid thus obtained at 100° under the ordinary pressure of the atmosphere, was stronger than that obtained by Graham from dilute sulphuric acid by heating it to the same temperature in a vacuum until it ceased to lose weight—the dihydrate $H_2SO_4,2H_2O$ remaining, showing the greater affinity for water possessed by the latter acid.

Selenic acid, concentrated as above described, was poured into the flask previously referred to, and gradually heated. Weak selenic acid commenced to pass over at 55°, evidenced by the potash liquefying and effervescing, owing to the presence of potassium carbonate which it contained, being the ordinary commercial potash. It was then heated slowly up to 100°, kept at that temperature so long as any acid distilled over, and the strength of the residue taken; 0·9432 grm. required for neutralisation 24·10 c.c. of seminormal soda solution, equivalent to 92·44 per cent of selenic acid. Subsequent to this experiment, acids heated on various occasions to 100° were found to have the following percentages of anhydrous selenic acid:—92·03, 92·08, 93·28, and 93·70; the different results being found due to the varying conditions of the experiments, such as the length of time of heating, the quantity of potash and its proximity to the acid, the amount of the latter and the size of the flask containing it.

The acid which had been heated to 100° was next heated to 150°. At the latter temperature the more or less dilute acid distilling over appeared in the form of dense white fumes resembling those of sulphuric acid. 0·6898 grm. of the residue left neutralised 18·42 c.c. of semi-normal soda solution, equivalent to 96·58 per cent of selenic acid. It was again heated to 150°, and kept at that temperature so long as any acid distilled over: 0·417 grm. of the residue left neutralised 11·21 c.c. of semi-normal soda, equivalent to 97·25 per cent of selenic acid.

A fresh portion of acid was heated to 155° and kept for some time at that temperature: 0·8045 grm. of the residue neutralised 21·72 c.c. of semi-normal soda, showing 97·67 per cent of selenic acid. It was next heated to 162°, and the strength of the residue taken: 0·7291 grm. neutralised 19·72 c.c. of semi-normal soda, equivalent to 97·85 per cent of selenic acid.

The same acid was then heated to 216°, and the residue obtained was allowed to remain in the flask during the night. In the morning it was found to be frozen into a crystalline mass so hard that it was necessary to use a steel chisel in order to remove portions for examination. When dissolved in water and tested it was found to contain some selenium dioxide. Trials were then made to ascertain if a lower temperature would produce a similar result without decomposition of the acid; 180° was found to be sufficient for the purpose, and the following course was finally adopted:—The acid which had been concentrated on the water-bath, as far as possible, was heated gradually in the flask to 100°, and kept at that temperature so long as any acid distilled over, the greater part of the water being thus removed. The U-tube was then disconnected, emptied, and re-filled with stick potash. The flask was next heated gradually to 180°, kept at that temperature until no more acid distilled over, and then immediately cooled. A still better arrangement was to use so little acid that it was unnecessary to change the potash. The acid was heated gradually and continuously up to 180°, allowing bubbles to pass slowly through it, as before described. When 180° was reached the potash was watched, and as soon as it ceased to be acted upon, the flask was immediately cooled. An hour or less was generally found sufficient time for a small quantity of acid.

A specimen obtained in this way was found, when examined, to be very free from selenium dioxide, a little of it diluted with water and saturated with hydrogen sulphide merely giving a faint colouration without any precipitate. Another portion was acidified with hydrochloric acid and barium chloride added; on boiling the filtrate with stannous chloride it only became darkened in colour without any precipitation of selenium. 0·6725 grm. was taken to estimate the strength. 18·54 c.c. of semi-normal soda were required for neutralisation, equivalent to 99·73 per cent of selenic acid; 0·724 grm. of another acid prepared in a similar way, but which contained rather more selenium dioxide than the last, required for neutralisation 19·94 c.c. of semi-normal soda, equivalent to 99·64 per cent of selenic acid. A portion of a third acid weighing 0·329 grm., was dissolved in water, barium chloride added, and also hydrochloric acid in order to prevent any selenious acid from precipitating. The resulting barium selenate weighed 0·6337 grm., equivalent to 99·75 per cent of selenic acid. As has been already mentioned, the acid employed contained an acid potassium selenate equivalent to 0·07 per cent of neutral sodium selenate found. Taking this into account, and calculating on the acid with the sodium selenate deducted, the three results become respectively—

I.	II.	III.
99·80	99·71	99·77

The difference between the above results and 100 per cent must be ascribed partly to the very hygroscopic character of the acid in the anhydrous condition, and consequent slight absorption of moisture during the process of weighing. It is necessary to observe, however, that in making the above calculations, and all through in this paper, 78·87 has been adopted as the atomic weight of selenium, the number given by Meyer and Seubert in their "Recalculations of the Atomic Weights." If 78·80, the number given in Clarke's "Recalculations," be taken, the three results become—

I.	II.	III.
99·75	99·66	99·72

Petersson and Ekman state that the results of a great many analyses show that the most probable atomic weight of selenium is 79·08 (*Berichte der Deutschen Chemischen Gesellschaft*, ix., 1210). If this number be taken, the above percentages become respectively—

I.	II.	III.
99·94	99·85	99·91

The results arrived at from the foregoing experiments lead to the conclusion that *at 180° in a vacuum, selenic acid parts with all combined water, and remains as the anhydrous acid*, H_2SeO_4.

It may be well here to summarise the precautions necessary to be taken in preparing the anhydrous acid, so far as we have ascertained them. They are briefly as follows:—To use for the purpose an acid as pure as possible, to have a thoroughly good vacuum, to avoid too high or prolonged heating, and to keep a sufficient quantity of solid potash in close proximity to the acid all through—which may be arranged by using a small flask, and having the tube leading from it short and wide.

(To be continued).

Enamelled Steel Dishes.—Messrs. Jones Brothers and Co., of Wolverhampton, have lately introduced dishes made of very thin sheet-steel, smoothly coated with highly glazed white enamel. The one before us is rectangular in shape, and has ridges along the bottom so as to fit it for photographic requirements, but the same kind of enamelled steel dish could easily be made of shapes and sizes to suit the chemical laboratory; and although we have not tested the glaze we should say that a glaze which is sufficiently resisting to stand the chemical agent used in photography would be of considerable use in many branches of chemistry.

NOTE ON A SEDIMENT DEPOSITED FROM A MIXTURE USED IN CALICO PRINTING.

By J. A. WILSON.

In the production of the Turkey-red discharge style a mixture is made for producing the yellow pattern, consisting of tartaric acid, lemon juice, and lead nitrate. On standing this liquor deposits the above sediment, consisting of lead and tartaric, citric, and other organic acids, probably from the lemon juice, since lemon juice contains 4 or 5 ounces of organic acids, not citric or tartaric, to the gallon.

An analysis of the sediment gave—

	Per cent.
Moisture	9·48
Tartaric acid	34·87
Citric acid	0·04
Other organic acids	6·01
Lead	46·66
Other matters and loss	2·94
	100·00

The Laboratory, Tottington,
April 16 1889.

SOME OBSERVATIONS OF THE INFLUENCE OF ADHESION AND SOLUTION ON AFFINITY.

By H. N. WARREN, Research Analyst.

The important influence of cohesion in preventing chemical action, and the manner in which the force of adhesion, as displayed in the production of solution, may act in favouring chemical action, are well known to those employed in analytical pursuits, frequently observed by the incautious addition of too strong an acid when employing barium nitrate as a precipitant for the sulphates. Since barium nitrate is soluble in dilute acid and water, but insoluble in a concentrated acid, when concentrated nitric acid is added to barium carbonate it occasions but a slight effervescence, which speedily terminates, although the acid may be in large excess. This may even be preserved for an indefinite time provided it be hermetically sealed in a glass tube; if the liquid, however, be diluted with a small quantity of water a brisk action is temporarily renewed, but again soon terminates. On a further addition it recurs, and eventually, on the addition of a sufficiency of water, the whole of the barium carbonate is decomposed and dissolved. For a somewhat similar reason several alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol. Thus, an alcoholic solution of tartaric acid will not decompose the carbonate of potassium.

An alcoholic solution of HCl is without action on potassium carbonate, but will decompose calcium carbonate. An alcoholic solution of nitric acid decomposes calcium carbonate but not potassium carbonate. The above-mentioned tartrates are insoluble in alcohol, so are potassium chloride and nitrate, but calcium chloride and calcium nitrate are freely soluble in that menstruum. Again, metallic magnesium will not decompose water at all ordinary temperatures, but if previously amalgamated with mercury, and the amalgam thus obtained be thrown into water, decomposition at once takes place. On the addition of ammonium sulphide to an alkaline solution containing a salt of nickel a dense black somewhat flocculent precipitate of nickel sulphide is produced, but on maintaining a slow current of sulphuretted hydrogen through a hot solution of nickel picrate, the sulphide is gradually precipitated upon the sides of the vessel containing the same in the form of a brilliant mirror, surpassing in appearance the finest quality of plumbago.

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A NEW AND EASY METHOD FOR THE RAPID AND SURE DETECTION OF MERCURY IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris),
Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

A student of modern mineralogy has neither the time nor the inclination to determine qualitatively the metallic and non-metallic elements of the minerals which are continually being brought under his notice by the tedious, if accurate, ordinary wet way analytical methods of the chemist. And yet it is of the utmost importance that he should be able to identify with perfect accuracy the elementary or simple substances of the naturally occurring raw materials of his science—but in the very shortest possible space of time. Accordingly, the most advanced mineralogists of to-day, in determining the composition of their ores and veinstones, very properly make use, as much as possible, of the rapid blowpipe methods of testing, such as heating, with and without fluxes and other chemicals, in partially closed tubes, in open tubes, on charcoal, platinum, aluminium, in borax, boracic acid, &c., &c. The whole department of blowpipe analysis, however, has been for the last score of years so sadly neglected, not only in this country and America, but also in Germany and Scandinavia, where its foundation was laid at the end of the last and the beginning of the present century, that the mineralogist is not unfrequently, against his will and the best interests of his science, forced to fall back, for confirmations at least, on the slow processes of present day analytical chemistry.

With the object in view of completing a working system of quick and certain determinations of elements, on the basis of Berzelius's and Plattner's blowpipe operations, the author has spent much time in carefully investigating the nature and reactions of the known tests, and where these have failed to give under all circumstances rapid and satisfactory results, in seeking for new ones to supply their places. As a result of this search for other and better means of identification two new tests have been discovered, one for antimony and the other for mercury.

An account of the former test has already been published in the CHEMICAL NEWS, vol. lviii., p. 296, and vol. lix., p. 15; to give a description of the latter is the object of the present communication.

This new method for the detection of mercury, which has been in operation in the author's laboratories for the last six months, depends on the fact that when a small quantity of iodine in the form of vapour, *newly liberated* from a compound, is allowed to impinge on metallic mercury, it instantly converts it into the characteristic scarlet mercuric iodide. The method of applying the test and the various preliminaries necessary in every case of blowpipe analysis are briefly detailed below.

The author may here mention that he has very carefully examined all known mercury minerals, and other minerals containing only the slightest trace of that metal, by his process, which in every case has rapidly yielded very satisfactory results.

The first operation in blowpipe analysis consists in heating in a narrow glass tube, closed at one end, first the powdered body *alone*, and afterwards, if the previous heating affords certain results, the same with the *addition of a flux*. A substance containing mercury yields, when heated by itself in the closed tube, a sublimate which is either metallic or non-metallic in character. Most com-

pounds of mercury are decomposed by heat alone, and so furnish, when subjected to a certain temperature, the former sublimate; but mercur*ous* chloride, and bromide, and mercur*ic* chloride and iodide, and to a certain extent the sulphide also, are volatile without decomposition, and accordingly produce sublimates of non-metallic lustre. All compounds of mercury, however, when dry and intimately mixed with three times their bulk of ordinary anhydrous fusion mixture ($K_2CO_3+Na_2CO_3$), yield, under the influence of heat, metallic mercury, which condenses on the cooler portions of the tube above the assay. This metallic sublimate, when unmixed with other matters (metallic or otherwise), and in large quantity, usually shows distinctly enough its characteristic globules; but when impure or small in amount the globular character is not at all evident, and it may then be quite easily mistaken for arsenic alone, and sometimes, though rarely, for antimony. In the latter case this new process will afford quick and certain means of determination, while in the former it should also prove useful, as trustworthy confirmation. If the substance, then, which is undergoing examination gives with, if not without the aid of flux, a metallic sublimate, pour into the tube two drops of concentrated nitric acid, and immediately afterwards a single drop of a fairly strong solution of potassium iodide in water. The nitric acid *at once* splits up the iodide of potassium, and the iodine is liberated in fumes which act on any mercury in the sublimate or in the assay, and *instantly* produce the unique scarlet iodide of mercury, which is largely thrown up against the sides of the tube. The antimony tri-iodide produced in like manner is brownish in colour, and becomes yellowish after exposure to the air for some little time. The arsenic tri-iodide is yellow, and this, as in the case of mercury, forms at once; but if the bottom of the tube containing the excess of nitric acid be heated slightly the fumes from that body quickly decompose the iodide, and a spongy dark grey mass of arsenic is driven all around the upper part, at least, of the tube. In the same way the nitric acid quickly decomposes the antimony iodide, while it does not act at all *nearly so rapidly* on the mercuric iodide. The table below shows perhaps more clearly how this test would be applied in the ordinary course of blowpipe analysis.

Table for the Detection of Mercury in Minerals.

a. Heat the powdered substance in a small piece of hard glass tubing (say with a ¼-inch bore) closed at one end.

1. A *metallic* sublimate is produced. Proceed further by *b*.

2. A non-metallic sublimate is formed. Heat a fresh portion of the substance *mixed* with about three times its bulk of fusion mixture. A metallic sublimate forms. Proceed further by *b*.

3. There is no evidence of the slightest volatilisation other than water. *No* mercury is present in the mineral.

b. Pour into the tube containing the metallic sublimate and assay *two* drops of strong nitric acid, then at once *one* drop of potassium iodide solution, and heat the bottom of the tube *a little*. A scarlet mass forms and remains on the sides of the tube. Mercury is present in the body tested.

Detection of VERY MINUTE *Quantities of Mercury.*

When the mercury occurs in very minute quantities the metallic sublimate described above may not be perceptible on the sides of the glass tube. In this case, when only the *merest traces* of mercury are looked for in the substance, proceed as follows:—Place in the closed tube, as already detailed, the mixture of powdered substance and flux, and introduce on the end of a stout wire a small piece of gold leaf, which should be held just over the surface of the mixture. Now apply heat for a minute or so. *Any* mercury present will be volatilised, and the vapour will combine with the gold to form a whitish amalgam. Take out the wire with the gold leaf on its end after sufficient heat has been applied to the mixture in the tube. Touch the surface of the leaf which faced the assay with a single drop of concentrated nitric acid, and on the top of this add immediately a drop of potassium iodide solution; the fine scarlet iodide will at once very distinctly appear on the amalgamated surface of the gold leaf if any mercury whatever was present in the body subjected to examination.

SEPARATION OF COPPER FROM LEAD, CADMIUM, MAGNESIUM, MANGANESE, MERCURY, ZINC, &c.

By G. VON KNORRE.

THE metals must be present as sulphates or chlorides. The solution, which, if necessary, is reduced to a small volume by evaporation, is neutralised with ammonia if free mineral acids are present, and acidified with a few drops of hydrochloric acid. It is then heated almost to a boil, and there is added an excess (five parts to about one of the copper present) of nitroso-β-naphthol, previously dissolved in boiling acetic acid at 50 per cent. It is convenient to filter the hot solution of nitroso-β-naphthol through a moistened filter and let the filtrate flow into the hot solution containing the metals, stirring meanwhile. After the liquid had stood for some hours in the cold the copper nitroso-naphthol is filtered off and washed with cold water until a drop of the filtrate, if evaporated on platinum foil, leaves no solid residue. The washings, even then, have a yellow colour which does not affect the results. When dry, the filter and precipitate are placed in a capacious tared porcelain crucible, the filter is closed, the crucible is loosely covered, placed upon a sheet-iron plate, and cautiously heated with a small flame until vapours no longer escape. The temperature is then gradually raised, and the crucible is finally ignited with access of air until the carbon is burnt off, when the copper oxide can be weighed. If the quantity of copper nitroso-naphthol is considerable, pure oxalic acid or ammonium oxalate should be added to the precipitate on incineration in order to secure quiet decomposition. In presence of silver the copper precipitate is argentiferous.—*Zeitschrift für Analytische Chemie.*

ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

IN the older forms of marine boilers, working at comparatively low pressures, sea water was almost universally employed; but with the introduction of high pressure tubular boilers the amount of deposit formed was so serious, and the difficulty of cleaning out the incrustation from between the tubes so great, that it became almost imperative to discontinue the use of the sea water, and to rather accept the expense of supplying the boilers with distilled water, than risk the burning and destruction of the tubes and plates in inaccessible portions, where the deposit had to be allowed to collect until the time could be spared for a complete clean out and refit. But, after several years' experience of this system, it is found that the trouble has only been transferred from the steam boilers to the distilling apparatus, and that the enormous deposits formed in the latter cause them frequently to

* Read at the Thirtieth Session of the Institution of Naval Architects, April 11th, 1889. Admiral Sir John Hay, President, in the Chair.

break down or become in some way or another unfit for use, so necessitating the introduction of sea water into the boiler to eke out the supply of distilled water from the condensers.

Under these circumstances, I have thought that it might be acceptable to bring before the members of this Institution the results of a series of experiments recently made in the laboratories at Greenwich, together with some suggestions founded upon them, which might be of value in attempting a solution of this very serious evil

I propose in this paper to show the nature and cause of the deposits formed from each class of water used in marine boilers, and then, by a study of the characteristic properties of each constituent of the incrustation, to arrive, if possible, at a method for its prevention.

The waters at present in use in marine boilers may be classified as—

1. Sea water.
2. Distilled water.
3. Mixtures of (*a*) sea water and distilled water; (*b*) sea water and fresh water.

By fresh water is here meant the water, either from spring, well, or river, which is taken on board when in port, and which, under certain circumstances, is used mixed with condensed water or sea water, in the boiler.

Such water is very variable in composition, but, as a rule, contains as its chief saline constituents the carbonates of lime and magnesia, held in solution by carbonic acid present in the water, and also small quantities of the sulphates of these metals, and traces of common salt.

Sea water contains a far higher proportion of saline matters in solution than fresh water, and also in totally different proportions, as although sea water is only river water concentrated by the evaporative power of the sun's rays during long ages, yet, owing to deposition during the flow of the water down rivers, and also to its being used by certain forms of marine life, calcic carbonate (carbonate of lime), which is the chief saline constituent of fresh water, is reduced to a mere trace in salt water, whilst the salt has become the all important constituent, and the sulphates of lime and magnesia, together with chloride of magnesium, are also present.

The wide difference in composition of fresh and salt water may be seen from the following analyses:—

Salts in Solution in River and Sea Water.
Grains per Gallon.

	River water. Thames.	Sea water. Lowestoft.
Calcic carbonate (chalk)	10·80	3·9
Calcic sulphate (gypsum)	3·00	93·1
Magnesic sulphate	0·25	124·8
Magnesic chloride		220·5
Magnesic carbonate	1·25	trace
Sodic chloride (salt)	1·80	1850·1
Silica (sandy matter)	0·56	8·4
Oxides of iron and alumina	0·27	trace
Organic matter	2·36	trace

Distilled water is presumably free from all dissolved solids, but the condenser water always contains some of the lubricants from the cylinder; and in the days of animal and vegetable lubricators, like fat and oils other than mineral, this water, on account of the super-heated steam breaking the oils up and liberating fatty acids, caused a large amount of damage to the plates of the boiler; but with the use of mineral oil lubricators of the right kind this trouble is done away with, and a slight coating of organic matter is, as a rule, the only incrustation found in a boiler using distilled and condenser water only.

The great difference existing between sea and fresh water would lead one to expect a wide difference also in the kind of deposit formed from them, and this is found to be the case, as the following analyses of incrustations formed in the boilers of steamers using fresh river water, the brackish water at the mouth of a river, and sea water respectively, show:—

	River.	Brackish.	Sea.
Calcic carbonate	75·85	43·65	0·97
Calcic sulphate	3·68	34·78	85·53
Magnesic hydrate	2·56	4·34	3·39
Sodic chloride	0·45	0·56	2·79
Silica	7·66	7·52	1·10
Oxides of iron and alumina	2·96	3·44	0·32
Organic matter	3·64	1·55	trace
Moisture	3·20	4·16	5·90
	100·00	100·00	100·00

These may be taken as typical deposits, and show that with fresh water the incrustation may be looked upon as consisting of calcic carbonate, with small quantities of other compounds; that with a mixture of fresh and salt water the deposit consists of nearly equal parts of the calcic carbonate and sulphate; whilst the sea water gives practically calcic sulphate.

The presence of calcic sulphate exercises a very marked influence upon the condition and physical properties of the incrustation, as, under the conditions in which it is formed in a boiler, it separates in a crystalline form, and binds the deposit into a hard mass, an action which is also aided by the presence of magnesic hydrate.

A deposit consisting of calcic carbonate only, or of calcic carbonate and traces of the oxides of iron and alumina, sodic chloride, &c., is separated as a soft powder, which remains suspended in the water for some time, and which can fairly easily be removed from the boiler on cleaning; whilst, if calcic sulphate is present, the scale is extremely hard, and generally requires the use of hammer and chisel to detach it from the plates and tubes, an operation which is extremely injurious, and tends to shorten the life of the boiler.

The three principal constituents of boiler incrustations may therefore be looked upon as calcic carbonate, calcic sulphate, and magnesic hydrate, and the causes which lead to their deposition must now be considered.

Calcic carbonate is practically insoluble in pure water, that is to say, it requires more than 10,000 parts of pure water to dissolve one part of the carbonate;* but carbonic acid, which is present in all natural waters, when in contact with calcic carbonate converts it into bicarbonate, which is soluble, and this forms the so-called "temporary hardness" in fresh waters. On heating such a water the bicarbonate is decomposed, carbonic acid gas escapes, and the calcic carbonate being insoluble, is deposited. Calcic carbonate is slightly more soluble in saline solutions, such as sea water, than in pure water, but the difference is so small that the above may be looked upon as applying equally to fresh and salt water.

Calcic sulphate is to the marine engineer the most important constituent of boiler incrustation, and its separation as a deposit from water is dependent upon a totally different class of phenomena to those which bring about the precipitation of the calcic carbonate. Calcic sulphate is dissolved in water by the solvent power of the water itself, and not through the agency of carbon dioxide, and therefore merely boiling water at ordinary pressures does not suffice to cause its deposition, and for this reason, it forms, together with soluble magnesium salts, the "permanent hardness" of fresh water.

The solubility of calcic sulphate in pure water varies very considerably with the temperature.

So that calcic sulphate is most soluble in water at 95° F. or 35° C.† roughly, one part of calcic sulphate being dissolved in 400 parts of water; and, inasmuch as the solubility of the salt is considerably decreased at 212° F.

* Soluble in 16,000 parts of pure water according to Brande; 12,858 according to Kremers; 16,000 to 24,000 according to Buchholz.
† Poggiale, *Ann. Ch. et Phys.*

100 parts of water, at a temperature of	Dissolve calcic sulphate.
32° F. or 0° C.	0·205
41° „ 5°	0·219
53·6° „ 12°	0·233
68° „ 20°	0·241
86° „ 30°	0·249
95° „ 35°	0·254
104° „ 40°	0·252
122° „ 50°	0·251
140° „ 60°	0·248
158° „ 70°	0·244
176° „ 80°	0·239
194° „ 90°	0·231
212° „ 100°	0·217

or 100° C., if a saturated solution be taken at 95° F. or 35° C., and is then heated to 212° F. or 100° C. a precipitation of a portion of the calcic sulphate will take place.

Calcic sulphate is much more soluble in a saline solution, such as sea water, than it is in fresh water, but its solubility rapidly decreases, (1) on concentration of the saline solution, and (2) on increase of temperature and pressure.

To trace the effect of concentration on the calcic sulphate a considerable volume of sea water was taken and slowly evaporated at ordinary atmospheric pressure, the composition of the water being ascertained by analysis, and the density of the water being taken at successive stages of the concentration.

Sea water having a density of 1·027 ($\frac{1}{32}$ salinometer) was allowed to concentrate by exposure to air until it had a density of 1·029, and it was then evaporated, and analyses made at the following densities :—

Saline Constituents per Cent.

Density	1·029	1·05	1·09	1·225
Sodic chloride	2·6521	4·4201	7·9563	23·8689
Calcic sulphate	0·1305	0·2175	0·3915	none
Calcic carbonate . ..	0·0103	0·0171	none	none
Magnesic carbonate ..	0·0065	0·0032	none	none
Magnesic chloride ..	0·2320	0·3865	0·6960	2·0880
Magnesic sulphate ..	0·1890	0·3150	0·5670	1·7010

The deposits formed during concentration were carefully collected and analysed, and it was found that the deposit formed up to the density 1·05 consisted of basic magnesic carbonate only. The deposit taking place between densities 1·05 and 1·09 consisted of—

Basic magnesic carbonate and hydrate	17·6
Calcic carbonate	82·4
	100·0

no trace of calcic sulphate having yet come down, whilst between the densities 1·09 and 1·225 the deposit consisted of pure calcic sulphate only, so that on the concentration of the sea water three distinct stages of deposition may be traced :—

1. Deposition of basic magnesic carbonate.
2. Deposition of calcic carbonate with remaining traces of the basic magnesic carbonate and hydrate, and, finally,
3. Deposition of the calcic sulphate.

If the sea water be heated and concentrated above a density of 1·225, the salt commences to crystallise out.

The deposition of the calcic sulphate during the concentration of the sea water is due to two causes; in the first place, although it is more soluble in a dilute solution of salt than in fresh water, yet it reaches its maximum solubility at a density of 1·033, and after this point concentration of the saline solution diminishes the amount which can be held in solution, and the calcic sulphate is perfectly insoluble in a saturated brine. The second cause for its deposition is the rise in boiling-point which accompanies the increase in density, the higher the temperature the less the solubility of the calcic sulphate, so that when a temperature of 284° to 302° F., or 140° to 150° C. is reached it becomes perfectly insoluble, both in sea and fresh water.

These experiments show that, if sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1·09), to prevent the deposition of the calcic sulphate; but any such regulation of the density is rendered abortive by the fact that pressure and consequent raising of the boiling-point acts upon the calcic sulphate in solution in exactly the same way as concentration and increased temperature, so that in the older forms of boiler, working even at a comparatively low pressure, most of the sulphate was deposited, whilst in the high pressure boilers now in use, if the water contains the smallest trace of calcic sulphate, it will be deposited; and, as any deposit formed amongst the tubes in such a boiler would be almost impossible to get at to clean away, it is practically impossible to use sea water in them, and they are supplied with the water from the condenser augmented by distilled water made in special distilling plant. The question has been raised as to whether, if sea water were mixed with distilled water so as to reduce its density very low, it would deposit the calcic sulphate; but experiment shows that, even if sea water is mixed with many hundred times its bulk of distilled water, the minute trace present is deposited under pressure when the temperature approaches 284° F. or 140° C. So that when, through a breakdown in the distilling apparatus, sea water has to be used with the condenser water in even very small quantities, slight scale is sure to be formed. When a saline solution containing calcic sulphate is heated under pressure or concentrated until calcic sulphate begins to separate, the sulphate will continue to precipitate even after the liquid has cooled down or the pressure has been removed; and, finally, when calcic sulphate has separated at a high temperature or pressure from sea water, even though the water has only the ordinary density (1·027), the rate at which the sulphate will re-dissolve is so extremely slow that the re-solution is practically nil.

These two last properties are due to the form in which the calcic sulphate separates from sea water under pressure. Calcic sulphate occurs in nature as gypsum in which each molecule of calcic sulphate is combined with two molecules of water of crystallisation: when calcic sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcic sulphate to one of water; whilst, after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a further change of crystalline form, loses all water, and becomes "anhydrite," which is pure calcic sulphate free from water of crystallisation, and it is this change in crystalline form which binds deposits containing it into such a hard mass.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1889.

Mr. William Crookes, F.R.S., Vice-President, in the Chair.

Messrs. J. L. Hoskyns-Abrahall, D. Carmody, C. J. McNally, M.D., C. Proctor, and W. J. Waterhouse were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Evans, care of Messrs. Savory and Moore, 86, King's Road, Brighton; William Taylor Gibbs,

Richmond House, Plaistow, Essex; Byron B. Goldsmith, 19, East 74th Street, New York City, U.S.A.; Charles James Grist, West View, Grange Road, Egham; Alfred Edward Tibson, 79, South Hill Park, Hampstead Heath, N.W.; Ignatius Singer, Nailsworth, South Australia.

The following papers were read:—

36. "*Sawarri Fat.*" By J. Lewkowitsch, Ph.D.

Sawarri nuts contain 63 per cent of a white solid fat, of which the author has determined the physical constants. The density is 0·8981 at 40° C. relatively to that of water at 15° C.; the melting-point lies between 29·5° C. and 35·5° C.; the solidifying-point at from 23·3° to 29° C. The acids from the fat melt at 48·3° C. to 50° C., and solidify at 47 to 46° C.

Saponification value (Köttsdorffer)	199·51	
Insoluble acids (Hehner's value)	96·91	p. c.
Glycerol determined by the acetin method .	9·14	,,
Free acids	2·4	,,
Mean molecular weight of the acids	272·8	,,
Soluble acids (Reichert's value)	0·65	,,
Iodine value of the fat (v. Hübl)	49·5	,,
Iodine value of the acids	51·5	,,
Acetyl value (Benedikt)	77·5	,,
Iodine value of the acetylised fatty acids ..	51·8	,,

The author intends to examine the acids in the manner indicated by Hazura.

37. "*Note on β-Phenylnaphthalene.*" By Watson Smith.

Zincke and Breuer (*Annalen*, ccxxvi., 23—60) and Zincke (*Annalen*, ccxl., 137—146) succeeded in synthesising β-phenylnaphthalene by the dehydration and condensation of styrolene alcohol—

$$2C_6H_5\cdot CH(OH)\cdot CH_2(OH) - 4H_2O = C_6H_4\begin{<}{CH:CPh \atop CH:CH}\end{>}.$$

β-Phenylnaphthalene melts at 101°, and is easily soluble in alcohol, ether, benzene, and chloroform; on oxidation with chromic anhydride in glacial acetic acid solution it yields a quinone which crystallises in fine bright yellow needles, melting at 110°; this quinone possesses the characteristic property of rapidly polymerising on exposure of its solution to light, an insoluble polymeride being precipitated. In 1879 the author obtained a phenylnaphthalene by passing a mixture of bromobenzene and naphthalene through a red-hot tube (*Chem. Soc. Trans.*, 1881, 546), and for reasons then fully stated, he considered it to be β-phenylnaphthalene. Zincke attempted to obtain the hydrocarbon by the author's method, but seems to have failed, as he gives it as his opinion that it cannot be prepared in this way, or, that if a hydrocarbon is formed, it must be α-phenylnaphthalene. The author's attention was recently called to these facts, and especially to the latter statement by Professor Schorlemmer, and he was thus led to attempt the preparation of Zincke's quinone from some of a fairly abundant stock of phenylnaphthalene still remaining. The result was that the conversion into the quinone by Zincke's method proceeded with the utmost ease, a product answering in every respect to the quinone described by that chemist being obtained, amply confirming the author's earlier conclusion that the phenylnaphthalene obtained by him was the β-isomeride.

The author cannot understand that any such difficulty as Zincke describes should arise in preparing phenylnaphthalene by the pyrogentic method. Three products are principally obtained after removing excess of bromobenzene, viz., naphthalene, dinaphthyl, and phenylnaphthalene; there may also be a minute quantity of diphenyl. Fractional distillation easily removes naphthalene and diphenyl, leaving phenylnaphthalene boiling at 345°, and dinaphthyl boiling above 440°. Boiling with somewhat dilute alcohol now extracts phenylnaphthalene, and leaves behind dinaphthyl, which is insoluble in this liquid. Usually a second sublimation is necessary to obtain a product melting at 101°, that first obtained melting at about 96° C.

Discussion.

Dr. Armstrong remarked that it was most probable that the original product was the α-derivative; the proof now advanced that the hydrocarbon obtained by Mr. Watson Smith's method was the β-compound was of interest, as affording an indication that isomeric change of the α- into the β-derivative took place at high temperatures.

38. "*Nitro-β-Chloronaphthalene.*" By Henry E. Armstrong and W. P. Wynne.

β-Chloronaphthalene is readily nitrated by dissolving it in its own weight of glacial acetic acid, and adding about 2½ molecular proportions of nitric acid ($d = 1·42$); the mixture is allowed to stand for two or three days. β-Bromonaphthalene behaves similarly. Nitro-β-chloronaphthalene crystallises from spirit in sulphur-yellow needles melting at 116°; on distillation with PCl_5 it yields the dichloronaphthalene melting at 63·5°, and is therefore the heteronucleal 1 : 2′ α-nitro-β-chloronaphthalene. On reduction it yields the corresponding amidochloronaphthalene. The authors are studying the sulphonic acids derived from this amine.

39. "*The Action of Halogens on Betanaphthol.*" By Henry E. Armstrong and E. C. Rossiter.

If betanaphthol be treated with a single molecular proportion of bromine it is converted, as shown by Smith, into a homonucleal-monobromo derivative, which presumably corresponds in constitution with 1 : 2 chlorobetanaphthol; if an excess of bromine be used, a tetrabromonaphthol is produced, and as this yields bromophthalic acid it contains one of its four bromine atoms in the second nucleus. The authors have sought to determine at what stage the bromine atom becomes introduced into the second nucleus.

By treating betanaphthol with two molecular proportions of bromine it is almost entirely converted into dibromobetanaphthol; this crystallises from acetic acid with one molecular proportion of the acid in prisms melting at 84°; the acid of crystallisation is spontaneously given off on exposure of the crystals. The pure substance crystallises from petroleum spirit in woolly needles melting at 106°. On oxidation with alkaline permanganate it yields bromophthalic acid; whence it follows that on introducing a second atom of bromine into betanaphthol it enters the non-hydroxylised nucleus.

The preparation of a tribromonaphthol appears to present difficulties, a mixture of di- and tetra-derivatives being usually obtained. Together with the bromonaphthols, relatively small amounts of yellow products are always formed, which probably correspond to the chlorinated keto-compounds described by Zincke.

When betanaphthol is submitted to the action of a single molecular proportion of chlorine, it yields but a relatively small amount of chlorobetanaphthol, the chief product being a resinous substance (Cleve); this result has found an explanation in Zincke's experiments, which show that chlorine tends to convert betanaphthol into additive keto-compounds. The authors find that a theoretical yield of chlorobetanaphthol (m.p. 69°) is obtainable by gently warming betanaphthol suspended in thrice its weight of carbon bisulphide with a molecular proportion of sulphuryl chloride, SO_2Cl_2. On attempting to prepare dichlorobetanaphthol by further treatment with SO_2Cl_2, little besides resinous matter was obtained; alphanaphthol, in like manner, when submitted to the action of two molecular proportions of the chloride, afforded a large amount of resinous matter. Chlorobetanaphthol is almost entirely converted by a single molecular proportion of bromine into a bromochlorobetanaphthol, corresponding to the dibromobetanaphthol previously described. It also crystallises with one molecular proportion of acetic acid in long prismatic needles melting at 92°; the pure substance sublimes in fine needles melting at 101°, but does not crystallise satisfactorily from any solvent.

Schaeffer's betanaphtholsulphonic acid is converted by bromine into a monobromo derivative, which may also be obtained by sulphonating Smith's bromobetanaphthol (Armstrong and Graham); the corresponding chloro-acid is readily formed on sulphonating chlorobetanaphthol, together with a small quantity of an isomeric acid yielding more soluble salts. The brom- and chlor-acids behave alike on treatment with excess of bromine, being converted into the bromhydroxynaphthaquinonesulphonate, $C_{10}H_3BrO_2(OH)\cdot SO_3H$, first described by Armstrong and Graham; a relatively very small proportion of dibromhydroxynaphthaquinone being also produced. Armstrong and Graham came to the conclusion that the bromhydroxysulphonate — which contains the bromine in the quinonic nucleus—was the final product of the action of bromine, but later experiments have shown that this is only the case when the experiment is made by treating Schaeffer's salt with bromine; if the pure bromhydroxyquinonesulphonate be used instead, the quinonic nucleus becomes destroyed and a sulphophthalic derivative is obtained. The hydrogen bromide produced in the formation of the quinone sulphonate from Schaeffer's salt, in fact, protects the former from oxidation.

Armstrong and Graham succeeded in obtaining only a small quantity of a dibromo-derivative from Schaeffer's acid, the tendency being for the action to extend at once to the formation of the quinonesulphonate; by brominating a solution of the potassium salt of Schaeffer's acid in muriatic acid, Armstrong and Streatfeild succeeded, however, in preparing a tribromo-derivative. Both the di- and the tri-bromo acid gave easily soluble salts, and, as on treatment with bromine, they were converted into quinone sulphonate, the bromine atoms are contained in the hydroxylised nucleus. By sulphonating the above-described bromochloro- and dibromobetanaphthols, the authors have obtained sulphonic acids, the salts of which are difficultly soluble, and which, on treatment with bromine, yield a large proportion of the dibromhydroxynaphthaquinone already mentioned; the production of this compound is confirmatory of the heteronucleal constitution of the two di-derivatives of betanaphthol. Bromochlorobetanaphthol yields two isomeric acids on sulphonation; it is noteworthy that neither these nor the acid from the dibromo compound yield Schaeffer's acid on reduction; as this acid is obtained on reducing the acids produced on sulphonating chloro- and bromobetanaphthol, it follows that the sulphonation of the mono- and di-derivatives of betanaphthol takes place in a different manner—it may be that, as in the case of betanaphthol, a sulphate is first produced, and that the subsequent isomeric change takes a different course; or perhaps a sulphate is formed in the case of the mono-derivative, while direct sulphonation is affected in that of the di-derivative. The authors are engaged in further investigating the sulphonic acids of the chloro- and bromonaphthols generally.

40. "*β-Methoxynaphthalenesulphonic Acids.*" By J. Percival, B.A.

It has been shown by Armstrong and Amphlett that if β-ethoxynaphthalene be sulphonated by means of chlorosulphonic acid without application of heat, a mixture of two sulphonic acids is obtained, one of which corresponds to Schaeffer's betanaphtholsulphonic acid; and that if the product be heated on the water-bath for a short time this latter acid is alone obtained, an isomeric change taking place. The author has undertaken a series of experiments with the object of determining whether any effect is produced by varying the radicle introduced in place of the hydroxylic hydrogen of betanaphthol; in the first instance he has studied the behaviour of β-methoxynaphthalene prepared from betanaphthol, and finds that there are very marked differences to be observed in the behaviour of the methoxy- and ethoxy-compounds.

The product obtained without application of heat chiefly consists of an unstable acid together with a relatively small proportion of a stable acid corresponding to Schaeffer's betanaphtholsulphonic acid; but after heating during a couple of hours on the water-bath the unstable acid is no longer present, having undergone isomeric change into the stable acid. If the aqueous solution of the unstable acid be heated nearly to boiling, the acid is decomposed, β-methoxynaphthalene separating; in this way it is easy to ascertain the amount of unstable acid in the original product of sulphonation. Even a solution of the barium salt of the unstable acid gradually undergoes decomposition when evaporated, β-methoxynaphthalene and barium sulphate becoming separated. No such behaviour was noticed in the case of the barium salt of the unstable ethoxy acid, although this salt was observed to decompose at about the temperature at which the water of crystallisation was expelled, 130—140°. On adding bromine to a solution of the unstable methoxy acid, a precipitate is at once formed consisting of tribromo-β-methoxynaphthalene; this crystallises from benzene, in which it is very soluble, in long slender white needles melting at 105°; no such precipitate is obtained from the unstable ethoxy acid.

The salts of the unstable acid are very soluble, the potassium salt crystallising in plates, which aggregate into nodular masses, containing half a molecular proportion of water. The salts of the stable acid are difficultly soluble; like the corresponding ethoxy acid, it is readily converted by bromine into a bromo-β-methoxysulphonate, and ultimately into bromhydroxyquinonesulphonate, identical with that obtained from Schaeffer's acid.

41. "*The Acids Formed by Displacing NH_2 in Brönner's Betanaphthylaminesulphonic Acid by Halogens.*" By W. Houlding, B.Sc.

Arnell has shown that two isomeric acids are formed on sulphonating β-chloronaphthalene, and subsequent experiments by Forsling and others have proved that these acids correspond to the Badische and Brönner modifications of betanaphthylaminesulphonic acid; the 1 : 2′ acid is the chief product, and the 2 : 3′ acid the minor product, especially if chlorosulphonic acid be employed as sulphonating agent. Armstrong and Wynne have shown that although the minor product when heat is not applied, the 2 : 3′ acid becomes the major product if after sulphonation the crude acid be heated during several hours at 150—160°; and they have consequently suggested that the 2 : 3′ acid is not a direct product of sulphonation, but results entirely from the occurrence of isomeric change. β-Bromo- and β-iodonaphthalene were each found in like manner to afford two isomeric acids, which it was to be presumed corresponded to those obtained from β-chloronaphthalene; but Armstrong and Wynne have pointed out as noteworthy that the melting-point of the sulphochloride of the iodo acid obtained as minor product was abnormally low, thus—

	Chlorosulphochloride.	Bromosulphochloride.	Iodosulphochloride.
Major product ..	130°	147°	174°
Minor „ ..	109	125	92·5

The author has therefore carefully compared the acids prepared from Brönner's 2 : 3′ betanaphthylaminesulphonic acid with those obtained by sulphonating β-chloro-, β-bromo-, and β-iodonaphthalene. As was to be expected, his results entirely confirm those of Forsling with reference to the identity of the chloro acid from Brönner's acid with the minor product of sulphonation of β-chloronaphthalene—that which affords a sulphochloride melting at 109°. It is noteworthy that both the chlorosulphochloride and chlorosulphobromide, m. p. 124°, yield the same sulphonamide melting at 183°, which is a proof of the non-occurrence of an isomeric change such as was observed by Gessner in the case of α-bromonaphthalenesulphonic acid. In like manner, the author finds that the bromo acid from Brönner's acid is identical with the minor product of sulphonation of β-bromo-

naphthalene: the salts of the acids are similar in appearance to those of the corresponding chlor acid, and are also all anhydrous; the sulphochloride melts at 124°; the sulphobromide at 118°: both sulphochloride and bromide yield the same sulphonamide, melting at about 204°. By distilling the bromosulphochloride with PCl_5 it is converted into a chlorobromonaphthalene, which crystallises in thin plates, melting at 137°; the corresponding dibromonaphthalene was obtained in small needles melting at 149°, but owing to the small amount at disposal this melting-point cannot be regarded as sufficiently determined. The iodo acid obtained from Brönner's acid was found to differ considerably from that obtained as minor product on sulphonating β-iodonaphthalene, the sulphochloride melting at 140° instead of 92·5°, and the sulphonamide at about 223° instead of 211°; the salts of the two acids also differ, the barium and sodium salts of that from Brönner's acid crystallising both in anhydrous plates and in monohydrated needles.

It appears therefore that on sulphonating β-iodonaphthalene either the initial change is the same as that which occurs on sulphonating the chloro and bromo compounds, and the consequent isomeric change follows a different course; or sulphonation is perhaps simultaneously effected in two different ways, neither iodo acid being the product of isomeric change.

With the object of determining the nature of the change experiments have been instituted with the iodo acids, corresponding to the three amido acids isomeric with Brönner's; the results will form the subject of a subsequent communication.

ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, Wednesday, May 1, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Vice-President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1888, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £81,000, entirely derived from the Contributions and Donations of the Members.

Forty-five new Members were elected in 1888.

Sixty-four Lectures and nineteen Evening Discourses were delivered in 1888.

The Books and Pamphlets presented in 1888 amounted to about 296 volumes, making, with 570 volumes (including Periodicals bound) purchased by the Managers, a total of 866 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuble services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President.—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer.—Henry Pollock.

Secretary.—Sir Frederick Bramwell, Bart., D.C.L., F.R.S., M.Inst.C.E.

Managers.—Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir James Crichton Browne, M.D., LL.D., F.R.S.; William Crookes, F.R.S.; Francis Galton, M.A., F.R.S.; Colonel James A. Grant, C.B., C.S.I., F.R.S.; The Rt. Hon. Sir Wm. R. Grove, M.A., D.C.L., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; David Edward Hughes, F.R.S.; Rev. John Macnaught, M.A.; William Henry Preece, F.R.S., M.Inst.C.E.; William O. Priestley, M.D., LL.D., F.L.S.; John Rae, M.D., LL.D., F.R.S.; William Chandler Roberts-Austen, F.R.S.; Lord Arthur Russell; Basil Woodd Smith, F.R.A.S.

Visitors.—William Anderson, M.Inst.C.E.; John Birkett, F.R.C.S.; Alfred Carpmael; Ernest H. Goold, F.Z.S.; Charles Hawksley, M.Inst.C.E.; John Hopkinson, M.A., F.R.S., M.Inst.C.E.; Victor Horsley, F.R.S., F.R.C.S.; Ludwig Mond, F.C.S.; Edward Pollock; Lachlan Mackintosh Rate, M.A.; Arthur William Rücker, M.A., F.R.S.; John Bell Sedgwick, J.P., F.R.G.S.; Thomas Edward Thorpe, Ph.D., F.R.S.; Thomas Tyrer, F.C.S.; James Wimshurst.

NOTICES OF BOOKS.

Thirteenth Annual Report of Her Majesty's Inspectors of Explosives: being their Annual Report for the Year 1888. London: Her Majesty's Stationery Office.

The first point to which the Inspectors draw attention, and with only too good reason, is "the unsatisfactory character of much of the work done by the Local Authorities and their officers, and the still more unsatisfactory and, in some instances, wholesale neglect of their duties by many of these authorities." The general condition of the factories and magazines inspected is by no means unsatisfactory. Some private establishments of this kind, it is said, may challenge comparison with any factories or magazines in other countries, whether public or private.

The total number of manufactories (under continuing certificate and license) is now 112, exclusive of "toy firework" factories. During the four years before the Act came into operation, 1871—74, the average fatality was 37.

Several new explosives have been added to the licensed list, namely, Fortis explosive, carbo-dynamite, carbonite, di-flamyr, securite, bellite, miner's safety explosive, E.C. Company's sporting powder, the same Company's rifle powder, socket (? rocket) light signals, Pain's instantaneous pyrotechnic fuzes, and priming tubes. The authorised definition of roburite has been twice altered.

Several new explosives have been submitted for examination. Of these, flameless securite, smokeless powder, and lithotrite passed. Bronolithe and silatvar are still under examination, and stone carbonate, matagnite, romite, safety gunpowder, Howittite, and nitrolactus were rejected.

In the factory of the New Explosives Company, Limited, at Penrhyndendraeth, in Merionethshire, serious illegalities were detected, *e.g.*, packing gun-cotton for conveyance in a Gladstone bag! Convictions were obtained in five of the six cases, but the penalties inflicted were utterly inadequate. Illegalities in small firework factories seem to be habitually committed, as the local officials do not take the trouble to study the provisions of the Order in Council. The manufacture of fireworks in private houses has been considerably diminished, and might, it is thought, have been entirely extinguished had the local authorities done their duty.

No case of the unlawful entry of a magazine has come to light during the year. Two stores, however, have been unlawfully broken open and portions of blasting-gelatin and of dynamite have been stolen. The Inspectors believe that explosives are very frequently conveyed by road without the precautions which the law demands. Such irregularities can only be detected by the local authorities. In one case a cart conveying a ton of gunpowder was sent through the Borough of Dudley in charge of a boy fifteen years of age. A box containing 2000 detonaters was on one occasion sent by railway with a false label so as to mislead the railway company as to the contents of the box.

In the special report of Dr. Dupré, chemical adviser to the Inspectors, it is mentioned that "Obertier's copper," an ingredient used in fireworks, is dangerous, as liable to spontaneous decomposition, in which chlorine compounds are given off. The paper tubes for the so-called pill-box

stars contain free sulphuric acid, due to the alum employed in the preparation of the paste. Of course, as Dr. Dupré does not fail to point out, the presence of free sulphuric acid along with chlorates is utterly inadmissible.

A fatal dynamite accident has some curious features. A miner had kept a cartridge of gelatin dynamite in his trousers pocket and omitted to remove it before his trousers were hung up to dry on the oven door of his cottage. The heat caused the cartridge to explode with fatal results to a lodger who was standing in front of the fire at the time! This is only one of the many instances of mischief from miners and quarrymen being allowed to carry explosives about with them, and take them to their dwellings. Common prudence demands that such perilous matter should remain in the custody of trustworthy officials and be served out to the workmen only when and as wanted for immediate use.

No serious instances of outrages with explosives, actual or intended, are recorded in the realm. A small charge of gunpowder was exploded, without doing any harm, close to a new small-pox hospital at Trooper's Hill, St. George, Gloucestershire. It was probably due to public indignation at the erection of a source of infection on what had been a public pleasure-ground. Several outrages are reported from the Continent. Four attempts have been made in Paris to blow up registration offices for café waiters, and the Police Station in the Rue de la Peile was similarly attacked. In the United States a plot was discovered to assassinate the judges, police, and witnesses who had been concerned in the prosecution of the Chicago anarchists, and a dynamitard was charged with attempting to throw a bomb at President Cleveland. Two explosions of blasting-gelatin took place in Fort Morbut and Fort Tarshyne, at Aden. A sentry was killed, some guns were dismounted, and their carriages were damaged. The Inspectors, from a consideration of the evidence, conclude that both these calamities were due to spontaneous decomposition in consequence of the high temperature. Mention is made of the fact that "high" explosives, commonly supposed incapable of exploding by mere ignition without a detonator, have sometimes been known to explode. Thus in an experiment at Lydd a ton of gun-cotton (in tins containing 2½ lbs. each) was set on fire; it exploded with startling abruptness and injured Sir F. Abel, who was only about 30—40 yards distant.

Into petroleum explosions, great and small, the Report does not enter fully; but it is mentioned that further legislation in connection with the storage and sale of petroleum is pending.

The impression left upon our minds by the examination of this Report is that the Inspectors are doing a very useful work, but that they are insufficiently backed up by the local authorities, and that the penalties inflicted for contravention of the Explosives Act are ridiculously trifling in view of the risk to life and property involved by such neglect.

The Art of the Assayer ("l'Art de l'Essayeur"). By A. Riche, Director of Assays at the Mint; Professor of Inorganic Chemistry at the Paris School of Pharmacy; Member of the Academy of Medicine. With the Co-operation of Edmond Gelis. Paris: J. B. Baillière et Fils.

The author defines the art of the assayer as "that portion of analytical chemistry which has for its object the qualitative and quantitative determination of the precious metals." As such, he enumerates gold, silver, and also platinum, which he states enters into the composition of a great number of trinkets. He includes also the determination of the metals which often accompany gold and silver and nickel, which have now become an article of commerce.

It must here be remarked that some authorities include under assaying all analytical operations performed in the dry way, whilst other writers speak of the assay of cinchona-bark, of opium, of guano, and of other organic compounds and mixtures.

The preliminary sections on apparatus and operations need not detain us. We remark merely that certain very convenient appliances for the production of heat by means of coal-gas do not appear to be mentioned.

The hydrometer recommended for determining the specific gravity of liquids is, of course, Beaumé, and the comparative table here given differs seriously from those commonly met with in standard works. Thus we generally find 76° B = sp. gr. 2·000, but here, 76° B = 2·116.

The processes given for the assay of the precious metals and their chief alloys are clearly described, illustrated where necessary, and are fully in accordance with the present state of chemical science. The author does not express any opinion on the possibility of a spectroscopic assay of the precious metals.

New Commercial Plants and Drugs. No. II. By T. Christy, F.L.S., &c. London: Christy and Co.

The substances here described are exclusively for medical purposes; hence, we cannot venture to pronounce any opinion as to their value; but certain statements made in the preface demand very serious consideration, and, we fear, contain too much truth. Mr. Christy, after complaining of the paucity of chemical and pharmaceutical research, says that "we have in Britain several institutions expressly and expensively fitted for the purpose? But what is the use of them if students are not taught to understand the value of original research? . . . The fault certainly lies at the door of those entrusted with the teaching of our students, and who, instead of encouraging them to take up original research, which is practically the best teacher of all, keep them bound down to the old fossilised lines, and render them practically useless as thoughtful workers."

Mr. Christy should throw in his influence with those who are combatting the examination system of education with all its corollaries. This is the real cause why we are not doing in every science what we otherwise could, and what we ought.

But we think he is mistaken when he intimates that researches carried out in Britain have to be published on the Continent before the English press will notice them. We think that both in pure and technical chemistry the amount of original work done in Britain and published in British journals and transactions is certainly not smaller than that which France has to show.

CORRESPONDENCE.

HYDROCYANIC ACID.

To the Editor of the Chemical News.

Sir,—I have found out that pure anhydrous hydrocyanic acid is obtained by passing dry arseniuretted hydrogen gas over dry potassium cyanide, gently heated,—

$$AsH_3+3KCN=3HCN+K_3As.$$

This is a much more economical way than using sulphuretted hydrogen and mercuric cyanide.

I have also discovered that arsenide of potassium or sodium is formed by passing dry arseniuretted hydrogen gas over dry, heated sulphide of potassium or of sodium—

$$2AsH_3+3K_2S=2K_3As+3H_2S,$$

or—

$$2AsH_3+3Na_2S=2Na_3As+3H_2S.$$

The previous book methods used the metals potassium or sodium; but it is easy to see that my way is much

more economical. It is necessary in all these three operations that the gas and solids be perfectly dry or the reaction does not take place.

I generally make my arsenious hydride by acting upon 1 part of zinc and 2 parts of white arsenic with hydrochloric or dilute sulphonic acid.—I am, &c.,

G. W. Blythe.

5, Alderley Road, Hoylake, Cheshire, May 1, 1889.

ACTION OF FERROUS SULPHATE ON SOILS.

To the Editor of the Chemical News.

Sir,—It would occupy too much of your valuable space to follow "X" in all his claims for Dr. Griffiths's experiments, but I think the following remarks show that Dr. Griffiths has *not* added *much*, if anything, to our previous knowledge.

In the oldest edition of "Johnston and Cameron" at hand just now (10th Edition, 1877, p. 394) they say:—"Ferrous sulphate applied in the form of a weak solution to sickly bleached plants has been observed to *change their colour to green and to improve their appearance generally. It has been applied to diseased trees.* Used in *large* quantities it is *poisonous* to vegetation." Dr. Griffiths's experiments commenced *after* 1880.

Every agricultural chemist knew, before Dr. Griffiths was born that all the copperases were germicidal, and that agricultural bluestone was, in great measure, green copperas.

Dr. Griffiths started with Amies' chemical manure, which, according to his own showing, consisted largely of copperas. Long before Dr. Griffiths worked upon it Amies, Co., said:—"As an insecticide (*sic*) it has great power in affording protection against the various parasitic destropers of vegetable life. It has been found to overcome the potato, vine, and cucumber diseases."

"X" and I are at variance in regard to the meaning attachable to a direct plant-food. A substance is not (in my opinion) a *direct plant-food* unless it is absorbed as such, and without decomposition by the plant, and afterwards elaborated in its tissues. Now, all properly conducted chemico-agricultural experiments go to prove that, wherever the conditions are such that green vitriol can be absorbed unchanged (through absence of aëration and cognate physical and chemical influences in the soil) by the plant, then such green vitriol is *plant poison*. But, on the other hand, where there the conditions are such that green vitriol, when applied to the land, may be oxidised and decomposed, then copperas can be profitably and safely used, just in proportion to the ability of the soil to decompose and alter it into harmless substances. Then green vitriol is an *indirect* plant-food.

Dr. Voelcker assigned the post of honour amongst the questions answered by soil analyses to whether or not the soil contained green vitriol, which, he said, occasionally occurs naturally in peaty and clayey soils—the very ones which want aëration, &c., thus supporting the view I have indicated.

When I do publish my agricultural experiments I shall invite criticism on the deductions I draw. I am sorry "X" is indignant at my having the audacity to criticise those of Dr. Griffiths.

"X" advises me, let me return the compliment. Cast French authorities aside and study the writers upon chemistry as applied to agriculture of your own country, from Lord Dundonald downwards.—I am, &c.,

John Geddes McIntosh.

Sulphuric Acid in the Air.—A medical contemporary alleges that 350 tons of sulphur are thrown into the air every winter day in London. This quantity represents upwards of 1000 tons of monohydrated sulphuric acid daily, not merely wasted, but employed in mischief.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 15, April 15, 1889.

The Late Prof. Chevreul.—In conformity with the very unusual wish of the family no *éloge* was pronounced at the funeral of the late illustrious *savant*, and the learned world is thus deprived of the appreciative surveys of his achievements, which some of his colleagues would have felt it an honour to deliver.

Researches on the Thionic Series.—M. Berthelot.—A thermo-chemical paper which does not admit of useful abstraction.

Experiments on Putrefaction and on the Formation of Farmyard Manure.—J. Reiset.—The author gives the details of his experiments mentioned in the last number of the *Comptes Rendus*. He believes that he has been the first to point out the abundant production of hydrogen carbide during the fermentation. During this anærobic fermentation the loss of nitrogen may become even more abundant than in slow combustion in the presence of oxygen.

On the Solubility of Salts. A Reply to M. Roozeboom.—H. Le Chatelier.—The author considers that the difference of opinion between M. Roozeboom and himself is much smaller than the former seems to suppose. M. Roozeboom has completely accepted the opinion that with every sudden change in the state of a solid salt which is dissolving there necessarily corresponds a sudden change in the track of its curve of solubility.

Speed of Transformation of Metaphosphoric Acid in Presence of Acids and Alkalies.—Paul Sabatier.—The author finds that the transformation is more rapid in presence of the strong mineral acids, such as the sulphuric and hydrochloric, whilst organic acids, such as the acetic, retard the phenomenon. With very small doses of sulphuric acid the accelerating influence is apparently null, or even negative at low temperatures. The more rapid destruction of the metaphosphoric acid is doubtless due to the temporary formation of dissociable hydrates, produced by the acids at the expense of the metaphosphoric acid. If saturated with an alkali the transformation of the metaphosphate into acid phosphate is imperceptible at 0°, very slow at 43·5°; prolonged boiling effects a complete transformation. In a liquid partially saturated we find the transformation slower than in the free acid, but more rapid than in an acid completely saturated. These results confirm the hypothesis formed as to the constitution of vitreous metaphosphoric acid. The chief reaction is a splitting up, which is effected less easily when the acid is saturated with a strong base.

Researches on Certain New Metallic Sulphides.—Arm. Gautier and L. Hallopeau.—The authors, on treating iron at a red heat with carbon disulphide, have obtained a sulphide, Fe_4S_3, a substance of a crystalline fracture and of a yellowish grey colour with bronze reflections. It can be filed and polished like soft iron. Its sp. gr. is 6·975. It is rather more magnetic than iron monosulphide. It undergoes no change on exposure to the air, and is not readily oxidised, even at a red heat. Weak acids dissolve it with an escape of hydrogen sulphide and hydrogen. If metallic manganese is heated to 1400° in the dry vapour of carbon disulphide it becomes covered with a black layer of MnS, a compound which has been obtained before in the crystalline state by another method. No subsulphide is formed. If manganese silicate (rhodonite) is treated at white-redness with the vapour of carbon disulphide a new compound is

obtained, Mn_3S_4. It decomposes water, evolving H_2S, and leaving a hydrated manganese oxide.

A Contribution to the Study of the Ptomaines.—Oechsner de Coninck.—The ptomaine $C_8H_{11}N$, if oxidised with potassium permanganate, yields the same pyridin-carbonic acid as does nicotin.

The Combustion-heat of Some Organic Bodies.—M. Ossipoff.—The author has made a thermo-chemical study of the cinnamic, atropic, and terebic acids.

On Calcium and Strontium Malonates.—M. Massol.—A thermo-chemical memoir not adapted for useful abstraction.

New Synthesis Effected by Means of Cyano-succinic Ether.—L. Barthe.—The author has obtained benzyl-cyanosuccinic ether.

The Determination of Organic Nitrogen by the Volumetric Method by Soda-Lime, and by Kjeldahl's Process.—L. L'Hote.—In the author's opinion the method of Kjeldahl does not afford the simplicity, the dispatch, and the accuracy of the soda-lime method. It gives figures comparable to those of the latter method when the acid liquid to be distilled is colourless. This transformation of the organic nitrogen into ammoniacal nitrogen is easy for crystalline substances, such as oxamide, caffeine, and urea, but it is not always possible, even after a considerable time, for many agricultural products. The methods of Dumas and of Will-Varrentrapp give approximately the same results.

No. 16, April 23.

The Nitroso-Compounds of Ruthenium.—A. Joly.—The author shows the existence of a very extended series of nitroso-ruthenium derivatives. He describes a nitroso-sesquichloride to which he assigns the formula $RuCl_3(NO)+H_2O$, and a nitroso-sesquioxide.

The Transformation of Nitro-Camphor into Nitroso-Camphor.—P. Cazeneuve.—The author has succeeded in transforming nitro-camphor into nitroso-camphor under a direct reductive action, heating chloro-nitro-camphor in aqueous alcohol with copper precipitated by zinc.

The Proportion of Gluten in Wheat.—E. Gatelier and L. L'Hote.—The authors' results seem to prove that the propertion of gluten in wheat may be increased by cultivation, and that it depends on the proportion of nitrogen to phosphoric acid used in the manure.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. v., No. 3.

Colorimetric Determination of Manganese: Assay of the Lead Peroxide used.—Prof. L. L. de Koninck.—The lead peroxide of commerce is prepared by treating an alkaline plumbic solution with a current of chlorine. This gas carries with it manganese chloride derived from its preparation, which, in contact with the alkali and the excess of chlorine, is converted into peroxide. Hence lead peroxide commonly contains manganese peroxide, and must of course be absolutely rejected in the colorimetric determination of manganese in steels. To detect manganese in lead peroxide in the moist way, a quantity of the product must be heated with an excess of undiluted sulphuric acid until the metals are converted into sulphates. On adding then with great caution a volume of water double or triple that of the acid used, then a fresh quantity of peroxide, and on heating for a few moments, if manganese is present the well-known colour of permanganic acid will appear.

Preparation of Chlorine Gas for Analysis.—Prof. L. L. de Koninck.—The author produces chlorine gas in the cold by the action of gaseous hydrochloric acid upon granulated pyrolusite. The gas is led up through a column of pyrolusite and the chlorine is dried by a passage over calcium chloride or pumice soaked in sulphuric acid.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 38.

Report Presented by M. Le Chatelier on Behalf of the Committee of Chemical Arts on the Alloy known as Delta Metal.—Delta metal, which is an alloy of 57 parts of copper with 43 parts of zinc and a few hundredths of foreign metals, is interesting on account of the ease with which it is forged and stamped at a dull red heat (500°), on account of its resistance, in which it approximates to steel, its immunity from atmospheric action, and its low price. The sole drawback which it presents is the difficulty of melting it without volatilising a part of the zinc.

Report Presented by M. de Luynes on Behalf of the Committee of Chemical Arts on M. Hélouis' Process for Colouring Metals for Embroidery.—No definite account is given of the process which M. Hélouis adopts for depositing thin films of metal upon textile fibres. He does not make use of electric action, but of heat.

Report Presented by M. Müntz on Behalf of the Committee of Agriculture on M. Milliau's Process for Detecting the Falsification of Olive Oil with Seed Oils.—In examining a suspected oil or fat, M. Milliau first liberates the fatty acids, and applies to them the special reagents required.

No. 39.

Report Presented by M. Bérard on Behalf of the Committee of Chemical Arts, on the Safety Papers and Inks presented by M. Schlumberger.—The author incorporates certain reagents with the stuff of the paper. No particulars of the safety inks are given.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.

TUESDAY 14th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Societyof Arts, 8. (Applied Art Section). "Venetian Glass," by Dr. Salviati.
—— Royal Institution, 3. "The Italian Renaissance Painters; their Employments," by Jean Paul Richter.

WEDNESDAY, 15th.—Meteorological, 7.
—— Pharmaceutical, 11. (Anniversary).
—— Society of Arts, 8. (Ordinary Meeting). "The Use of Spirit as an Agent in Prime Movers," by A. F. Yarrow.

THURSDAY, 16th.—Royal, 4.30.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8.
—— Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
—— Sanitary Institute, 5. "Fires and Fire-escapes, and the Prevention and Arrest of Fires," by H. E. Davis.

FRIDAY, 17th.—Royal Institution, 9. "Optical Torque," by Professor Silvanus P. Thompson.

SATURDAY, 18th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.

TO LAWYERS AND LAW STUDENTS.
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THE CHEMICAL NEWS.

Vol. LIX. No. 1538.

A NEW, EASY, AND RAPID METHOD OF DETECTING MINUTE QUANTITIES OF IRON IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris).
Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

By means of a good strong flame, produced in the ordinary way by the mouth blowpipe, heat for a minute or two a small portion of the mineral, preferably in a powdered condition, on *clean* platinum foil, with about four times its bulk of potassium nitrate or chlorate. The platinum should be heated from below, as it is not desirable that the flame should touch the assay. After the mass has been ignited as stated, add to it, *before it has cooled down*, by means of a piece of glass tubing, *pure* concentrated nitric acid drop by drop, until a single drop remains not dried up. Next pour on to the top of the unevaporated nitric acid, also by means of a narrow glass tube, two or three drops of an aqueous solution of potassium sulphocyanide. A *distinct* red colouration will immediately arise and remain if any iron was present in the mineral examined. As this test is extremely delicate, nitric acid quite free from iron must be obtained; and it is essential that the potassium nitrate or chlorate should also be pure. The platinum foil must be perfectly clean, and the dropping tubes must be rinsed with water before and immediately after the application of each test.

AN APPARATUS SUITABLE FOR LECTURE PURPOSES, TO ILLUSTRATE THE INFLUENCE OF PRESSURE ON THE VOLATILISING POINT OF ICE, AND OTHER PHENOMENA.

By Professor SYDNEY YOUNG, D.Sc.

It was first observed by Carnelley that when a block of ice with a free surface for evaporation is exposed to pressures lower than 4·6 m.m. it cannot be melted, no matter at how great a rate heat is supplied to it by radiation.

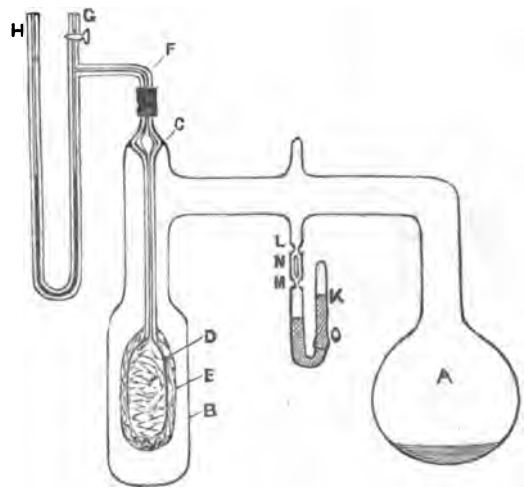
At a meeting of the Owens College Chemical Society eight years ago I suggested that the maximum temperature to which ice can be heated under any given pressure lower than 4·6 m.m. could be ascertained from the curve representing the vapour-pressures of ice at different temperatures, just as the boiling-point of water under any pressure is given by the curve of vapour-pressures of water (*Nature*, 1881, p. 239).

In 1883 Dr. Ramsay and I proved experimentally that this is the case, and we determined the temperatures of volatilisation of ice and other solids, obtaining in the following year an experimental proof of the fact previously predicted from thermodynamical considerations by Prof. Kirchhoff and Prof. James Thomson, that the vapour-pressure of a substance in the solid state at a temperature below its melting-point is lower than that of the substance in the liquid state at the same temperature.

Inasmuch, however, as a good pump is required to reduce the pressure sufficiently, and as the experiment by which these facts are proved is in other respects rather troublesome, it has not, I believe, been usually admitted in an ordinary course of lectures.

It seems possible, therefore, that an apparatus which I have constructed to illustrate the effect of pressure on the volatilising-point of ice may prove useful to other lecturers, more especially as it serves to illustrate some other interesting points. The apparatus is a modification of Wollaston's cryophorus and of that employed by Dr. Ramsay and myself in our investigations. The bulb, A, is similar to that in the cryophorus, but in place of the second bulb there is a wide cylindrical tube, B. At C is fused a tube of narrow bore (say 1 m.m.), to which is sealed a wider tube, D, closed at the end. This tube contains air, and acts as an air thermometer; it is covered with cotton-wool, which is to be saturated with water before beginning the experiment. The narrow tube is open at the upper end, and is connected by an indiarubber tube with the gauge, F G H, which contains sulphuric acid coloured with indigo as an indicator. The gauge is open at both ends, but is provided with a stopcock at G.

As in the cryophorus, the apparatus must be absolutely free from air, and the cotton-wool should be well washed with alcohol and ether to remove all grease, otherwise it may be difficult to saturate it with water. The pressure in the apparatus may be indicated by a mercury gauge, K, but obviously both the construction and the manipulation of the apparatus are rendered somewhat less easy by the addition. The gauge, if added, should have a circular



construction at L and a flattened construction at M, a narrow tube, N, closed at both ends, being placed in the tube between the constrictions. When the apparatus is in its usual vertical position the little tube, N, rests on the flattened constriction, and there is free communication between the gauge and the rest of the apparatus; but when, in the transference of water from one bulb to the other, the apparatus is inverted, the tube, N, falling against the circular constriction, closes the tube and prevents the escape of mercury from the gauge. For further security an air or vapour trap may be placed at O.

Description of Experiment.—The cotton-wool is thoroughly saturated and the rest of the water is then transferred to the bulb, A. The gauge is connected with the air thermometer and the stopcock closed. The bulb, A, is then immersed in a beaker of water cooled by a little ice; the diminution of pressure in the apparatus, consequent on the lowering of temperature, is at once indicated by the mercury gauge, and as the boiling-point of water is lowered by reduction of pressure, the temperature of the air thermometer is at once seen to fall. (The bulb, B, may be heated by boiling water or to any desired temperature during the whole experiment). When, by further addition of ice, the temperature of the bulb, A, sinks to 0° the pressure in the apparatus—if air has been completely

expelled—falls to 4·6 m.m., and the temperature of the air thermometer becomes constant. The stopcock is then opened so that the sulphuric acid may be at the same level in both limbs at this temperature, which is afterwards shown to be 0° C.

If we now replace the beaker of ice and water by a freezing-mixture at −5° the pressure in the apparatus will be still further reduced, and the temperature of the air thermometer will again fall, but the water will not freeze. We can therefore show—I find with perfect certainty—the cooling of water below 0° without freezing, and also the reduction of the boiling-point of water below 0°.

When the temperature is still further reduced by substitution of a colder freezing-mixture the water in A solidifies, and it will be seen that after the temperature of the air thermometer has fallen a little lower for a moment or two it suddenly rises to the zero-point already determined. After remaining constant for some time, until the whole of the water on the cotton-wool is frozen, the temperature falls rapidly, and it is now found to depend solely on that of the bulb, A, even though the bulb, B, be strongly heated.

A third determination of the zero-point may lastly be made, if sufficient ice remain on the cotton-wool, by removing the freezing-mixture. The temperature of the air thermometer slowly rises to 0°, and remains again at that temperature until the ice is melted.

The following facts are therefore clearly demonstrated by means of this appparatus:—(1) That the vapour-pressure of water (and of ice) depends on the temperature, and that the boiling-point (or the maximum temperature to which water with a free surface for evaporation can be heated) depends on the pressure; (2) that the vapour pressure of water at 0° is 4·6 m.m., and that under a pressure of 4·6 m.m. water boils at 0°; (3) that the boiling-point may be reduced below 0°, the water remaining liquid, but that when solidification begins the temperature suddenly rises and remains constant for a considerable time (it is assumed that this temperature is 0°); (4) that the volatilising-point of ice, like the boiling-point of water, depends on the pressure, and that if the ice has a free surface for evaporation the walls of the vessel surrounding it may be strongly heated without affecting its temperature.

Many of these points may be proved, though not in all cases so directly, without the mercury gauge. The apparatus is a little troublesome to construct, but, once made, the experiments may be conducted with almost as much ease, and with quite as much certainty, as that with Wollaston's cryophorus.

University College, Bristol.

SEPARATION OF IRON FROM CHROMIUM, MANGANESE, NICKEL, ZINC, &c.

By G. VON KNORRE.

In neutral and faintly acid solutions of ferric salts iron is precipitated by nitrosonaphthol quantitatively as ferri-nitrosonaphthol, $(C_{10}H_6O.NO)_3Fe$. In this manner iron can be separated from the above metals as well as from aluminium. The precipitation of the iron, which must be present as ferric sulphate or chloride, is effected in the same manner as the separation of copper. Small quantities of ferrous oxide do not prevent the quantitative separation of iron. To about 0·1 grm. of iron present at least 1 grm. of nitrosonaphthol should be used. If considerable quantities of free acid are present ammonia is added until a precipitate begins to appear, which is then re-dissolved in a few drops of hydrochloric acid. The washing and incineration are conducted in the manner described for copper, but the filter must not be too small, as the iron precipitate is very voluminous. The weight taken for analysis must be so small that not more than 0·3 grm. iron is present, as otherwise the bulk of the ferrinitrosonaphthol is too considerable.

The separation of iron and manganese gives very good results. In order to determine the manganese in the filtrate the liquid is concentrated by evaporation, rinsed into a capacious Erlenmeyer flask, and mixed with ammonium chloride and ammonia in large excess. The manganese is then precipitated by Nic. Wolff's method by means of a current of air charged with bromine. It falls as hydrated peroxide. The washings retain to the end a slight yellowish colour, but the results are not affected.

The separation of iron from zinc and from nickel presents no difficulty. In the filtrates zinc is precipitated with sodium carbonate and nickel with bromine-water and pure potassa-lye as nickel sesquihydroxide.

If a solution of chromium oxide containing acetic acid is mixed with a solution of nitrosonaphthol in acetic acid the liquid remains clear at first, but on heating to a boil there appears a red precipitate of chromonitrosonaphthol insoluble in water. Hence, if iron is precipitated by nitrosonaphthol in presence of chrome the results are too high.

Iron and chrome may be separated by acidulating the liquid with hydrochloric acid, as small quantities of this acid do not prevent the quantitative precipitation of iron. To 103 c.c. of the solution containing iron and chrome 5 c.c. of hydrochloric acid are sufficient, and the precipitation is conducted exactly as already described. The chrome in the filtrate cannot be perfectly precipitated by ammonia. The original liquid must therefore be diluted in a measuring-flask to a known volume. The iron is determined in an aliquot portion by means of nitrosonaphthol, and in a second chrome and iron are jointly precipitated by ammonia, when the proportion of chrome is found as difference.

In precipitating iron by means of nitrosonaphthol it is accompanied, not only by copper and cobalt, if present, but also by phosphoric acid.—*Zeitschrift für Analytische Chemie.*

RESEARCHES ON THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C., Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C., Demonstrator of Chemistry, R.C.S.I.

(Continued from p. 220).

Properties of Anhydrous Selenic Acid.

ANHYDROUS selenic acid is a white crystalline solid melting at 58° to a colourless oily-looking liquid. When thoroughly melted it remains in a super-fused state, and usually requires to be cooled to about 5° with constant stirring before it again freezes. The temperature then rises rapidly to 58°, and remains then stationary until complete solidification of the acid has taken place. When at rest it can be cooled lower than 5° without freezing, and it will remain in a stoppered bottle for months, and during frosty weather, in a liquid condition. It instantly solidifies at any temperature below 58° if a crystal of the solid acid be dropped into it, and it freezes sometimes at ordinary temperatures when rubbed with a sharp piece of glass or with the point of a pipette. It thus exhibits the property of super-fusion in a remarkable degree, and to a greater extent than anhydrous sulphuric acid, which, according to Marignac, possesses eminently the property of super-fusion (*Annales de Chimie et Physique* (1853), 39, 184). Its melting-point, 58°, is higher than that of anhydrous

* A Paper read before the Royal Society, May 2, 1889.

sulphuric acid, 10·5°, but lower than that of telluric acid, which may be heated nearly to redness without melting.

Anhydrous selenic acid crystallises in long interlacing hexagonal prisms. In an impure condition from the presence of selenium dioxide and other substances, its melting-point is lowered; and under those circumstances it is sometimes deposited slowly and spontaneously in the form of double pyramids, many of them intersecting in pairs.

Although much has been written upon the freezing-point of sulphuric acid, but little information appears to be published regarding its crystalline form. It is stated, however, in "Graham's Chemistry," vol. i., that the most concentrated acid when frozen often yields regular six-sided prisms of a tabular form. Chaptal describes the crystals as being six-sided prisms, terminating in pyramids with six faces. Both accounts agree in placing them in the hexagonal system. In order to see if the appearance of the crystals agreed with either of the above descriptions, some sulphuric acid was strengthened by boiling for some time, and then cooled down until it froze. The crystals obtained were found to be long six-sided prisms ending in pyramids, as described by Chaptal, and no prisms of a tabular form were observed. It is thus interesting to find that both anhydrous sulphuric and selenic acid crystallise in prisms in the hexagonal system, but it remains doubtful whether or not they are strictly isomorphous.

Selenic acid in the anhydrous condition possesses a powerful affinity for water, absorbing it quickly from the atmosphere. Their combination is attended with contraction and considerable evolution of heat, but less so than in the case of water and sulphuric acid. Like the latter, it disintegrates and blackens many organic substances, such as cork, indiarubber, &c. From others it withdraws the elements of water; thus, alcohol heated with it yields ethylene, and glycerin, acrolein. On cellulose it has an action similar to that of strong sulphuric acid, paper being converted by it into a tough parchment-like substance. For this reason it should not be filtered through filtering paper, except when cold and very dilute. Iodine dissolves in the super-fused acid when heated, forming a brown-coloured solution. It is acted on violently by pentachloride of phosphorus in the cold—a reaction which we are at present examining. Oxychloride of phosphorus also acts strongly upon it when warmed slightly, the reaction being attended with copious evolution of gas and reduction, apparently, to lower compounds. Selenium dioxide dissolves in it when heated, but the greater part crystallises out again in the cold. There is no evidence of formation in this way of an acid analogous to hyposulphuric acid, $H_2S_2O_6$. The crystals of the solid acid dissolve in strong sulphuric acid and also in Nordhausen acid.

The specific gravity of the super-fused acid, taken with a Sprengel tube at 15°, was found to be 2·6083. The specific gravity of the solid acid was taken in pure benzene of specific gravity 0·8851, which is not acted upon by it in the cold, and in which it is insoluble. As might be expected, it at once blackens commercial benzene. Its specific gravity, taken in this way, proved to be 2·9508 at 15°. It thus resembles anhydrous sulphuric acid in being denser in the solid than in the liquid state. The specific gravity of the liquid acid is much greater than that of anhydrous sulphuric acid, 1·8384; and on the other hand, the specific gravity of the solid acid is less than that of anhydrous telluric acid, which is stated by F. W. Clark to be 3·425 at 18·8° (*Silliman's American Journal* (3), 14, 281; 16, 401).

Monohydrated Selenic Acid: its Preparation and Properties.

Some selenic acid, which had been concentrated on the water-bath, was heated for some time in a vacuum at 100°, and its strength determined: 0·7858 grm. neutralised 20·00 c.c. of semi-normal soda solution, equivalent to 92·08 per cent of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 88·96 per cent, corresponding to a monohydrated acid, H_2SeO_4,H_2O. It was then poured into a wide tube, and its temperature gradually lowered, the same precautions being taken as to stirring and admission of air as were adopted previously in freezing out the anhydrous acid. Its viscosity increased with the fall in temperature, until at −32° it froze into a mass of crystals. These were melted and re-crystallised several times, and the resulting product examined.

A few of the crystals obtained were long needles, but most of them were large and broad, having a general aspect to which the term "glacial" might be applied appropriately, but differing in appearance under the microscope from those of glacial sulphuric acid.

Its melting-point was found to be 25°. Like glacial sulphuric acid, and also like anhydrous sulphuric and anhydrous selenic acid, when once melted it exhibits the property of super-fusion, and to as great an extent as the last-mentioned acid, since it may be cooled to more than 50° below its melting-point with constant stirring before it again freezes. When frozen, it remains quite solid at ordinary temperatures; but if the bottle containing it be removed to a warm room, or much handled, it commences to melt. Like the anhydrous acid, it at once freezes at any temperature below its melting-point when a crystal of the same acid is dropped into it. It resembles the anhydrous acid also in having a melting-point much higher than sulphuric acid of the same strength, that of glacial sulphuric acid being given by Pierre and Puchot as 7·5°, by Jacquelin as 8°, and by Marignac as 8·5°. It resembles the latter acid in having a melting-point lower than its anhydrous acid, but while the difference is about 2·5 in the case of sulphuric acid, the melting-points of the two selenic acids differ by 33°. In the following table their melting-points are compared:—

	Anhydrous.	Monohydrated.
Sulphuric acid	10·5°	8°
Selenic acid	58°	25°

It may be well to state here that 0° is given erroneously in several chemical works as the melting-point of anhydrous sulphuric acid. Marignac, the most recent investigator who has studied the subject, assigns the temperature 10·5° as its true melting-point.

The super-fused monohydrated selenic acid has a specific gravity of 2·3557 at 15°. That of the solid acid was taken in pure benzene, in which it is insoluble, and on which it is without action at ordinary temperatures, even after standing all night. A portion of the liquid acid was poured into the specific gravity bottle, a crystal dropped into it, and the acid, having become firm and cold, weighed, and the bottle filled with benzene. The specific gravity was found to be 2·6273 at 15°. It thus resembles the anhydrous acid in being denser in the solid than in the liquid state; while melting, the crystals sink rapidly in the liquid portion.

This acid commences to boil at 205°, the acid vapour given off being at first very weak, but it increases in strength with the rise in temperature. A more dilute acid is stated to behave in a similar manner, giving off nothing but water until the boiling-point reaches 205°—210°, at which temperature it has the strength of the monohydrated acid, H_2SO_4,H_2O.

The ease with which an acid of this strength can be obtained and crystallised supplies a means of separating impurities from selenic acid, all that is necessary to do being to boil a dilute acid until the temperature reaches 205°, cool, and drop in a crystal from an acid already frozen; the resulting crystals can then be melted and re-crystallised.

It may be well here to draw attention to the conflicting statements which are made in various works regarding the crystalline form of glacial sulphuric acid. "Watts's Dictionary," vol. v., and Richter's "Inorganic Chemistry," state that it crystallises in six-sided prisms; but in

several chemical works the crystals are described as rhombic prisms, while Pelouze and Fremy mention that it forms large transparent crystals which are rhomboidal prisms. The crystalline form is thus referred to three different systems. The first description is probably copied by mistake from that of the anhydrous acid. The most recent investigators of the point are Jacquelain (*Annales de Chimie et Physique* (1850), 30, 343), and Pierre and Puchot (*Annales de Chimie et Physique*, (1874), 2, 164). The latter say that the crystalline form appeared to them to be the oblique rhomboidal prism, and that they obtained the crystals, some very large, others thin and very long. Jacquelain describes them as being oblique prisms very inclined and very large; and states that he obtained them, by a rather slow crystallisation, distinctly oblique and very short, and by a quick crystallisation, in very long oblique prisms.

The Existence of Higher Hydrates.

A portion of dilute selenic acid was concentrated on the water-bath and its strength taken: 0·8603 grm. neutralised 19·48 c.c. of semi-normal soda solution, equivalent to 81·92 per cent of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 80·11 per cent, corresponding to a dihydrated acid, $H_2SeO_4,2H_2O$, and its temperature then gradually lowered. When kept at $-51°$ for some time it became as viscous as thick syrup, but did not freeze. The last acid was then diluted to a strength of 57·32 per cent of selenic acid, corresponding to a hydrate of the composition $H_2SeO_4,6H_2O$. The acid thus prepared did not freeze when kept at $-49°$, and was quite liquid at that temperature.

Although no proof of the existence of higher hydrates than the monohydrated acid was obtained in the foregoing experiments, it appears probable that a dihydrated acid, and perhaps other hydrates, are capable of existing. Sulphuric and telluric acid have both been obtained as dihydrates. Considerable heat is evolved when monohydrated selenic acid is mixed with sufficient water to reduce its strength to that of a dihydrated acid. When the latter is further diluted, there is an additional slight evolution of heat. It is probable that as the freezing-point of monohydrated selenic acid is considerably below that of the anhydrous acid, so the freezing-point of a dihydrated acid is still lower. In order to get an approximate idea of the amount of water which anhydrous selenic acid absorbs, a portion weighing 0·9776 grm. was placed on a watch-glass protected from dust, but with free access of air. After 24 hours the acid weighed 2·0284 grms., showing an absorption in that time of between eight and nine molecules of water by one molecule of anhydrous acid. Another portion weighing 0·4416 grm. was exposed until it ceased to absorb water; the acid then weighed 1·8152 grms., indicating absorption of rather more than 25 molecules of water by one molecule of anhydrous acid. Having arrived at this stage, it commenced to give off a little of the water which it had previously taken up, but the weather became warmer just at this period, so that probably the above amount does not represent the total absorption of which the acid is capable. It is less, however, than the amount taken up by the molecule of sulphuric acid, which is variously stated at from 80 to 100 molecules of water.

(To be continued).

New Metals.—According to the *Chemiker Zeitung* (Coethen), at the last sitting of the Russian Mineralogical Society K. D. Chrustschoff demonstrated the existence of a new metal which he has just discovered, and to which he gives the name Russium. It approximates closely to thorium, and is one of the bodies whose existence was foreseen by Prof. Mendeleeff. We learn also that Dr. Krüss has named the metal which he has detected along with nickel and cobalt Gnomium.

NOTE ON THE

SOLUBILITY OF WHITE PRECIPITATE IN SOLUTION OF AMMONIA CONTAINING AMMONIUM CARBONATE.

By G. STILLINGFLEET JOHNSON.

On testing a solution of mercuric chloride with some ammonia-water, which had been kept in the laboratory for many weeks in a loosely-stoppered bottle, a white precipitate was formed which dissolved easily without heat in excess of the reagent. This unusual reaction was traced to the presence of ammonium carbonate, which had been formed in the solution of ammonia by absorption of atmospheric CO_2.

On subsequently examining the influence of solution of ammonium carbonate in modifying the solubility of white precipitate, I found that this salt is far more powerful than ammonium chloride in preventing precipitation of mercuric chloride solution by ammonia. Not only does the addition of ammonium carbonate to ammonia-water cause resolution of white precipitate as fast as it is formed when mercuric chloride is added little by little; but, even after complete precipitation of a solution of mercuric chloride by ammonia-water, the addition of ammonium carbonate causes the precipitate to re-dissolve.

Chemical Laboratory,
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ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.*

By Professor V. B. LEWES, F.C.S., F.I.C.,
Royal Naval College Associate.

(Concluded from p. 224).

The presence of magnesic hydrate in boiler deposits has given rise to many theories to account for its formation, the most generally accepted one being that it is due to the mutual decomposition of water and magnesic chloride, which gave rise to magnesic hydrate and hydrochloric acid, the action being accelerated by the presence of metallic iron.

When sea water is evaporated with a large surface of metallic iron present in it, no free chloride can be detected in the distillate until four-fifths of the solution has been distilled over, whilst if the sea water be evaporated alone, it can be taken nearly to dryness without any decomposition. There is no doubt, however, that at a high temperature under pressure in marine boilers this decomposition takes place, but only to a very small extent, some of the deposit of the magnesic hydrate formed being due to the decomposition of the trace of magnesic carbonate first deposited from the water, in contact with the heated tubes, whilst the formation of the bulk of the magnesic hydrate present is explained by the following experiments. A sample of freshly precipitated and carefully washed calcic carbonate was boiled for some hours with a dilute solution of magnesic chloride and the steam led through baryta water. After a quarter of an hour carbon dioxide (carbonic acid gas) was freely evolved and gave a dense precipitate, whilst at the end of the operation the solution in the flask contained a large proportion of the calcium as calcic chloride, and the precipitate remaining was mostly magnesic hydrate. The same experiment was repeated, using sea water instead of the made up magnesic chloride solution, with exactly the same result.

In this reaction, taking place in a boiler, the magnesic chloride and calcic carbonate mutually react upon each

* Read at the Thirtieth Session of the Institution of Naval Architects, April 11th, 1889. Admiral Sir John Hay, President, in the Chair.

other, soluble calcic chloride and magnesic oxide are formed, and the magnesic oxide uniting with water forms magnesic hydrate, which is precipitated, carbon dioxide escaping.

This explains many points which the former theory leaves untouched—for instance, the fact of calcic carbonate being absent from marine boiler deposits, or, if present, in only very small quantities; and also that chloride of iron is not found in the water of the boiler, which would be the case if any corrosion or pitting was due to the action of free hydrochloric acid.

In many analyses of boiler deposits no magnesic hydrate is returned, but considerable proportions of magnesic carbonate, which naturally would be formed by the magnesic hydrate absorbing carbon dioxide on exposure for any length of time to the air.

Sodic chloride, magnesic chloride, and sulphate are not found as usual constituents of boiler scale; but in cases of heavy incrustation, pockets are found in the deposits filled with microscopic crystals of these salts which have slowly filtered in solution into cavities in the incrustation, and have been deposited there on evaporation of the liquid.

In some heavy deposits the method of formation of the incrustation can be clearly traced, and affords an insight into the changes which must take place in it after deposition.

A sample of incrustation attached to a tube cut from the boilers of H.M.S. *White Swan*, and which had, during three years' service on the East Indian station, completely filled up the spaces between the tubes in an inaccessible portion of the boiler, showed, on cutting a section, that two distinct forms of deposit could be traced; on the sides of the tubes a hard crystalline deposit of a fibrous structure had formed, whilst filling in the spaces between these highly crystalline layers was a softer kind of deposit, soft and loose on the exterior, but resembling alabaster in the interior, where not in contact with air.

A portion of the crystalline deposit from the upper surface of the tube was taken, carefully freed from any of the less crystalline part, and was analysed, giving—

Calcic sulphate	93·90
Silica	5·16
Sodic chloride	0·27
Moisture	0·67
	100·00

The silica was evidently fine sand which had settled out from shore water, and the moisture had most probably been absorbed from the air, so that this crystalline layer was practically pure calcic sulphate. The soft, outer portion of the second deposit which had evidently been formed by the action of air, on analysis, gave—

Calcic sulphate	89·33
Silica	0·52
Magnesic carbonate	6·49
Water	3·66
	100·00

and the inner portion on the surface of which the above had formed, selecting a portion free from pockets or cavities, gave—

Calcic sulphate	84·27
Magnesic hydrate	7·04
Silica	1·94
Oxides of iron and alumina	1·10
Water	5·65
	100·00

Whilst a portion containing a cavity in which were microscopic crystals, gave—

Calcic sulphate	46·06
Sodic chloride	38·66
Magnesic hydrate	4·16
Silica	1·09
Oxides of iron and alumina	0·65
Water	9·38
	100·00

The dual nature of the incrustation was even more marked in a specimen of heavy deposit got from the back of the boilers of H.M.S. *Northumberland*, and which could only be got whilst she was undergoing a thorough refit, and had been probably forming from three to six years, during which period she had been mostly in the Channel. The boilers had been worked at a pressure of about 65 lbs., and jet condensers used. The hard crystalline portion gave—

Calcic sulphate	91·31
Magnesic hydrate	1·77
Sodic chloride	1·39
Oxides of iron and alumina	0·12
Moisture	5·41
	100·00

Whilst the increase of magnesic hydrate was very marked in the non-crystalline portion—

Calcic sulphate	79·76
Magnesic hydrate	5·02
Sodic chloride	4·29
Calcic carbonate	0·97
Oxides of iron and alumina	0 52
Silica	1·10
Moisture	8·34
	100·00

The crystalline crusts of calcic sulphate are always thickest and purest, and, for this reason, hardest in contact with the tubes or plates of the boilers where they have been most heated, but one also finds these layers throughout the deposit, in many cases having a nodular form; and I think this goes to prove that after the deposit has come down as a mud, the calcic sulphate being as deposited already in small dense crystals, sinks through the lighter portions, and forms first a thin, and eventually a thick coating, which, by continuous heating under pressure, changes its crystalline form, giving up moisture, and becomes "anhydrite," whilst the deposit above it gradually becomes thicker and thicker, and more crystallisation of the calcic sulphate takes place, pieces of mill scale and other foreign substances present in the mud forming nuclei round which the "anhydrite" crystallises; the lighter portions, consisting of magnesic hydrate and traces of calcic carbonate, settling into any spaces that remain, and completing the deposit.

These deposits may be taken as a fair example of the incrustations formed by sea water in marine boilers, and, as before pointed out, the admixture of fresh river water would only alter its characteristics by increasing the proportion of calcic carbonate and magnesic hydrate present.

When distilled water only is used, a slight coating is formed, practically consisting only of organic matter, whilst if at any time through a break-down in the distilling apparatus sea water is mixed with the distilled water, a thin and very hard scale of calcic sulphate is formed. An incrustation of this character gave on analysis:—(See Table, next column).

This scale is of great interest from the presence in it of the carbonate of copper. It is well known that distilled water has a far greater solvent effect upon metals than a water containing salts in solution, and it is quite conceivable that the distilled water from the surface con-

Calcic sulphate	90·84
Magnesic hydrate	0·75
Sodic chloride	1·41
Silica	0·85
Copper carbonate	1·11
Oxides of iron and alumina	0·24
Organic matter	2·96
Moisture	1·84
	100·00

densers attacks the brass and copper tubes and fittings, and deposits the copper on the tubes of the boiler, although only in small quantities; and it is interesting to note that the green spots due to the presence of the copper are all on the under side of the scale, that is, in contact with the metal of the boiler tubes, showing that in all probability it had been deposited, as suggested, from the water in the boiler, and in contact with the iron would set up local galvanic action and tend to produce pitting.

A scale of this character is not as rule very thick, in the case quoted being only one-sixteenth of an inch in thickness in the tubes, and three-sixteenths of an inch on the crown of the furnace.

The importance of preventing boiler incrustation, and thereby saving the enormous waste of fuel and injury which it entails, has not been without its effect upon the minds of inventors, and almost every conceivable substance, from potato paring to complex chemical reagents, have from time to time been patented for this purpose, but they have all more or less failed for marine boilers, because either they have had an imjurious effect upon the metal of the plates, or else have produced an enormous bulk of loose deposit which, although easily cleaned out if the various parts of the boiler were accessible, and if it were only being used intermittently, yet in a marine boiler continuously working, rapidly chokes the portions between the tubes, and brings about an even worse state of affairs than that originally existing.

For these reasons, no treatment of sea water in the boilers themselves is practically possible, and with high pressure tubular marine boilers the water used must either be condenser water made up to the required bulk with distilled water, as is at present done, or else the condenser water must be augmented by sea water specially prepared for the purpose in a separate apparatus before being supplied to the boilers; and it is to this latter method I wish now to specially call your attention, as the high solvent action of distilled water upon metals and the cost of its production are primary objections to its use, whilst the constant breaking down from choking of the distilled water apparatus generally ends in the admixture of sea water with the condenser water and the formation of scale in the boilers.

From the data I have brought before you, and from the conditions under which the incrustations are formed, it is evident that if water is boiled under a pressure of 70 lbs., all the calcic sulphate and the carbonates of lime and magnesia will separate out, and by heating water to such a pressure for an hour in an auxiliary vessel, I have experimentally proved that water is obtained which will yield no further deposit when used in the marine boiler. The drawbacks to this process, however, would be that a strong boiler would be required to stand the necessary pressure, and that inasmuch as the deposits formed in this auxiliary boiler would be of the same kind as in the old marine boilers, it would necessitate constant stoppages for cleaning out, as from the binding and hardening effect of the calcium sulphate no mere blowing off would get rid of it, and in the method for treatment of sea water which I should suggest to you, we can take advantage of chemical as well as mechanical means for the separation of all salts in solution which are liable to produce deposits.

In all the more successful of the anti-incrustators sodic carbonate plays the most important part; indeed, several well-known and much-used articles of this class for fresh water boilers are only soda disguised by some cheap colouring matter and sold at a high price, and they act by converting calcic sulphate into calcic carbonate; sodic sulphate, a salt nearly as soluble as the sodic chloride itself, being at the same time formed, and the calcic carbonate precipitates as a soft powder, and there being no caicic sulphate to harden it, it can readily be got rid of.

From time to time the use of sodic carbonate in marine boilers has been advocated, but the serious drawback to its use is that it throws down the magnesium salts as carbonates, and so forms a bulky precipitate which, unless got rid of within a few weeks of its deposition, bakes to a hard mass and forms a bad form of deposit.

In order to separate the whole of the calcium and magnesium salts present, it is only necessary to raise the sea water to the boiling-point with the right quantity of soda solutions, and after separation of the precipitate formed the sea water will contain nothing but sodic chloride and sodic sulphate, both of which are so soluble that there is no fear of anything depositing, unless the solution were evaporated to a density of 1·2, a degree of concentration never approached in a marine boiler even when sea water was used without admixture of condenser water, except on the rarest possible occasions.

The sea water treated as proposed would have a density of 1·026, about $\frac{1}{2}$ on the salinometer, and would be mixed with the condenser water, which would in the proportions usually taken further reduce this to 1·002, and inasmuch as several tons of freshly prepared water would be daily inserted into the boiler, it would take very many months before an objectionable degree of concentration was reached, so that an occasional blowing off of the boiler when in port is all that would be necessary to entirely eliminate the question of density.

The mixture of condenser water and treated sea water would be far preferable to use in marine boilers to the mixture of condenser water and distilled water, as the action of the distilled water on the plates is done away with by the presence of the saline matter in solution, whilst the cost would be a quarter of that at present incurred for distilled water.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. G. C. McMurtry and H. H. Robins were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George William Howard, 3, Monson Terrace, Tunbridge Wells; Edward Wightman Bell, Spalding; Frederick Charles Knight, Trinidad, Colorado, U.S.A.; D. O'Mahoney, Queen's College, Cork; Benjamin Phillips, Oriental Bank Buildings, Bombay; Emanuel Roberts, Moratua, Ceylon; Robert M. W. Swan, 15, Walmer Crescent, Glasgow.

The following papers were read:—

42. "*Thiophosphoryl Fluoride.*" By T. E. Thorpe, F.R.S., and J. W. Rodger, Associate of the Normal School of Science, South Kensington.

This gas, the existence of which was announced by the authors in 1888 (*vide Trans.*, liii., 766), may be made by the action of arsenic trifluoride on thiophosphoryl chloride, or by heating a mixture of bismuth trifluoride, or better, lead fluoride, with phosphorus pentasulphide.

As the gas is readily acted on by the air or by moisture, and is decomposed at a moderately high temperature, it is necessary to take certain precautions in the preparation

if it is wished to obtain it pure. The air in the apparatus should be displaced by dry nitrogen, and the mixture should be heated in a leaden vessel to a temperature not exceeding 250°. The gas has no action on dry mercury, and may be stored in a glass gas-holder.

Analyses and determinations of its vapour-density showed that it possesses the formula PSF_3.

It is a transparent colourless gas, which, under a pressure of 10 to 11 atmospheres at ordinary temperatures, condenses to a colourless mobile liquid.

It is spontaneously inflammable in air, burning with a greyish green flame, forming phosphorus pentafluoride, phosphorus pentoxide, and sulphur dioxide, thus:—

$$10PSF_3+15O_2=6PF_5+2P_2O_5+10SO_2,$$

and spontaneously explodes with oxygen.

When heated or subjected to electric sparks it is decomposed with separation of sulphur and phosphorus, and formation of phosphorus trifluoride, and eventually phosphorus pentafluoride. If the heating is effected in a glass tube at a sufficiently high temperature the gas is ultimately converted into silicon tetrafluoride.

It has no action on oil of vitriol, carbon bisulphide, or benzene. It is soluble to some extent in ether; the solution burns with a greenish flame. Water gradually decomposes it, forming sulphuretted hydrogen, phosphoric acid, and hydrogen fluoride,—

$$PSF_3+4H_2O=H_2S+H_3PO_4+3HF.$$

On shaking the gas with a moderately strong solution of alkali it is absorbed with the formation of a thiophosphate and a fluoride. Thus, with caustic soda,—

$$PSF_3+6NaOH=Na_3PSO_3+3NaF+3H_2O.$$

The gas combines with gaseous ammonia to form a solid product, in accordance with the equation—

$$PSF_3+4NH_3=2NH_4F+P(NH_2)_2SF,$$

and the product is acted on by water, thus:—

$$2NH_4F+P(NH_2)_2SF+H_2O=$$
$$=2(NH_4F)HF+P(NH_2)_2HSO,$$

forming ammonium fluoride, hydrogen fluoride, and thiophosphodiamic acid. On treating the solution with copper sulphate, copper sulphide is ultimately formed, and the filtered liquid gradually deposits a crystalline salt of a bluish green colour, consisting of a double phosphate and silicofluoride of copper, $Cu_3P_2O_8{\cdot}CuSiF_6$.

43. "*The Boiling-point of Sodium and Potassium.*" By E. P. Perman.

Sodium and potassium were boiled in a hollow iron ball, which was heated by means of a blowpipe; the temperature was found in each case by means of an air thermometer, consisting of a glass bulb with a capillary stem which was lowered into the vapour, sealed, and broken open under water. The mean result for sodium was 742°, and for potassium 667°.

44. "*Note on the Heat of Neutralisation of Sulphuric Acid.*" By S. U. Pickering.

The heat of neutralisation is affected by the proportion of water present, and this latter should, theoretically, be infinite. By means of Thomsen's determinations of the heat evolved on diluting the solutions concerned, we can calculate approximately the values of the heat of neutralisation in infinity of water. The values for 2HCl and H_2SO_4 thus become 27,416 and 30,477 cal., instead of 27,480 and 31,380 cal., as they are when 200 H_2O is present; but Thomsen's results on the dilution of sulphuric acid were not extended sufficiently to show an abrupt change which occurs at the extreme end of the curve, and, when the correction is deduced from a more extensive series of experiments which the author has performed, the value for sulphuric acid becomes reduced to 28,197 cal., a value within experimental error, the same as that of hydrogen chloride.

45. "*α-ω-Diacetylpentane and α-ω-Dibenzoylpentane.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D.

Acetobutylbromide and ethylic sodacetoacetate interact readily when warmed together in alcoholic solution with formation of ethylic α-ω-diacetylcaproate,—

$$COMe{\cdot}(CH_2)_4{\cdot}CH(COMe){\cdot}COOEt.$$

This compound is a colourless oil, boiling at 238—242° (220 m.m.); when treated with an absolute alcoholic solution of ammonia it yields a crystalline compound, $C_{10}H_{15}NO_2$, melting at about 235° with partial decomposition. It is readily hydrolysed by warm alcoholic potash, yielding α-ω-diacetylpentane, together with smaller quantities of ω-acetylcaproic acid and acetic acid.

α-ω-Diacetylpentane, $COMe{\cdot}(CH_2)_5{\cdot}COMe$, crystallises in waxy plates, melts at 48—49°, and boils at about 213° (under 300 m.m. pressure) without decomposition. It combines with hydrogen sodium sulphite, forming a waxy seemingly amorphous compound, which is decomposed when warmed with water.

By treating the diketone in the cold with excess of hydroxylamine hydrochloride and potassium carbonate it is converted into the dihydroxime,—

$$CMe(NOH){\cdot}(CH_2)_5{\cdot}CMe:NOH;$$

this separates from a mixture of benzene and light petroleum in the form of a crystalline powder, melting at 84—85°.

ω-Acetylcaproic acid, $COMe{\cdot}(CH_2)_5{\cdot}COOH$, crystallises in colourless plates, melts at 29—30°, and, when pure, distils under reduced pressure with only slight decomposition. The silver salt, $C_8H_{13}O_3Ag$, crystallises from boiling water in colourless plates.

By warming an alcoholic solution of acetobutylbromide with ethylic sodomethylacetoacetate, ethylic α-methyl-α-ω-diacetylcaproate, $COMe{\cdot}(CH_2)_4{\cdot}CMe(COMe){\cdot}COOEt$, is obtained as a colourless oil boiling at 255—260°, (200 m.m.). It yields α-methyl-α-ω-diacetylpentane, $COMe{\cdot}(CH_2)_4{\cdot}CMeH{\cdot}COMe$, when hydrolysed with alcoholic potash.

Ethylic α-ω-dibenzoylcaproate,—

$$COPh{\cdot}(CH_2)_4{\cdot}CH(COPh){\cdot}COOEt,$$

is obtained by treating benzoylbutylbromide with ethyl sodobenzoylacetate in alcoholic solution. It is quickly hydrolysed when boiled with alcoholic potash, yielding α-ω-dibenzoylpentane, ω-benzoylcaproic acid, and benzoic acid.

α-ω-Dibenzoylpentane, $COPh{\cdot}(CH_2)_5{\cdot}COPH$, crystallises from dilute methyl alcohol in long needles, melting at 67—68°. The dihydroxime,—

$$CPh(NOH){\cdot}(CH_2)_5{\cdot}CPh:NOH,$$

prepared by treating an alcoholic solution of the diketone at the ordinary temperature with hydroxylamine hydrochloride and potash, crystallises from methyl alcohol in small glittering needles, and melts at 175—176°.

ω-Benzoylcaproic acid, $COPh{\cdot}(CH_2)_5{\cdot}COOH$, crystallises from light petroleum in long transparent plates, melting at 81—82°. The silver salt, $C_{13}H_{15}O_3Ag$, is a colourless, seemingly amorphous compound, almost insoluble in water.

The authors are at present engaged in investigating the behaviour of diacetyl- and dibenzoyl-pentane towards reducing and dehydrating agents. Very interesting results have been obtained, an account of which they hope to be able to lay before the Society at an early date.

46. "*Acetopropyl- and Acetobutyl-alcohol.*" By Harold G. Colman, M.Sc., Ph.D., and W. H. Perkin, jun.

In a previous communication to the Society (*Trans.*, li., 702) it was shown by one of the authors that acetobutyl-alcohol, obtained by boiling methyldehydrohexonecarboxylic acid with water, differs very widely from the substance of that name previously obtained by Lipp (*Ber.*, 1885, 3280) by boiling ethylic ω-bromopropylacetoacetate with dilute aqueous hydrogen chloride: the boiling-point of the former being 227°, whereas the latter product distilled at 154—155°—a difference of 70°.

In a paper published some time since (*Ber.*, 1888, 2138) "On the Action of Sodium on Ethylic Monochloracetate," Fittig and Erlenbach, in describing a substance boiling at 128°, which they supposed to be acetoisopropylalcohol, took occasion to state that the acetobutyl- and acetopropyl-alcohols previously described by the authors, could not possibly have the constitution assigned to them —owing to their syrupy consistency and high boiling-points—and that the description given by Lipp of his acetobutylalcohol agreed much better with the properties such a substance might be expected to possess. In a later paper (*Ber.*, 1888, 2647) these chemists discovered that their compound was not acetoisopropylalcohol, but was simply acetolethyl ether, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OC_2H_5$. As, however, in spite of this they did not withdraw their previous remarks on the nature of acetobutyl- and acetopropyl-alcohol, and as the authors had extensively used these substances in the synthesis of ring-derivatives, and drawn important theoretical conclusions from the results obtained, they have thought it necessary to again carefully examine these alcohols with a view to further establishing their identity.

In the first place they carefully repeated Lipp's experiment and found that the acetobutylalcohol obtained by him did in reality contain a considerable quantity of this substance, and that the product on distillation apparently boiled at 154—155°. Subsequent experiments showed, however, that this temperature, instead of being the boiling-point, was in reality the decomposing-point of the alcohol; the reason for this being, that the slightest trace of impurity is sufficient to prevent acetobutylalcohol from distilling without the most rapid decomposition into its anhydride (methyldehydrohexone) and water, the thermometer remaining constant at 154—155°. Lipp's acetobutylalcohol, when not too impure, can be distilled with slight decomposition under reduced pressure; the boiling-point noticed in two cases being 157° under 100 m.m. pressure, and 171° under 177 m.m. pressure; on distilling acetobutylalcohol from methyldehydrohexonecarboxylic acid under the same conditions, almost identical boiling-points were noticed.

Pure acetobutylalcohol was obtained from Lipp's crude product by distilling with steam, fractionating the methyldehydrohexone thus obtained, and dissolving it in water. In this way a thick oil was obtained which distilled under ordinary pressure at 225—227°, and was in every respect identical with the acetobutylalcohol from methyldehydrohexonecarboxylic acid.

These and other experiments, an account of which will be given later on, prove conclusively that acetobutylalcohol, when pure, boils at 225—227°, and not at 154—155° as stated by Lipp. Acetopropylalcohol behaves in every respect, physically as well as chemically, as the lower homologue of acetobutylalcohol, and as this substance gives levulinic acid on oxidation, no further experiments in proof of its constitution are necessary.

THE ROYAL SOCIETY.

THE following is a list of the principal exhibits at the Conversazione on May 8th, 1889.

The Tintometer.—Invented and exhibited by Mr. J. W. LOVIBOND, of Salisbury.

An instrument for matching, measuring, and recording the tints and hues of coloured solids and liquids, available for Eggertz's and Nessler's tests, valuation of pigments, standardising coloured solution, &c., &c.

The comparison of the coloured substances under examination with the standard tints and hues is made by means of an extensive series of accurately graded glass slips of different hues and strengths of colour.

Portable Cavendish Apparatus for Demonstrating the Attraction of Gravitation.—Exhibited by Mr. C. V. BOYS, A.R.S.M., F.R.S.

This apparatus differs only from the well-known apparatus of Cavendish in matters of detail. First, instead of the beam six feet long carrying heavy weights, used by Cavendish, or half a metre long, used by Cornu, the beam consists of a piece of lead only one centimetre long, and this is enclosed in a round tube of metal, outside which the attracting weights are placed. This reduction of size has been rendered possible by the use of quartz threads, the production of which was shown two years ago. The advantages gained by the reduced dimensions are increased sensibility and almost perfect elimination of temperature disturbances. The particular apparatus exhibited is designed to show the effect, and that it is the same from time to time, rather than to determine the constant of gravitation absolutely. By arranging the two attracting weights and the two ends of the attracted body at different levels, the deflection is nearly double.

Experiment Showing the Insulation of Quartz.—Exhibited by Mr. C. V. BOYS, A.R.S.M., F.R.S.

A pair of gold leaves are supported by a short rod of quartz which has been melted and drawn out about three-quarters of an inch. The atmosphere is kept moist by a dish of water. Under these circumstances a glass insulating stem allows all the charge to escape in a second or two. With the quartz, but little change is observed in four or five hours. The quartz may be dipped in water and put back in its place with the water upon it. It insulates apparently as well as before.

Apparatus for Testing the Elasticity of Fibres.—Exhibited by Mr. C. V. BOYS, A.R.S.M., F.R.S.

One of these pieces of apparatus consists of a microscope cathetometer arranged vertically, and a gravity bob which is deflected by the vertical pull of the fibre on a side arm. The lower end of the fibre is made fast to a beam carried by the microscope. A scale, to which the upper end of the fibre is fixed, is viewed by the microscope, which thus shows the stretch of the thread; the pulling force is found by subtracting the stretch from the vertical movement of the microscope, and multiplying by a constant previously found. The second piece of apparatus is used to measure the fatigue of fibres after torsion.

Fractures from Casting and Forgings of Manganese Steel, containing from 10 per cent to 36 per cent Mn, Illustrating the Influence of Different Combinations of Iron and Manganese.—Exhibited by Mr. R. A. HADFIELD.

When the manganese exceeds about 12 per cent, notwithstanding the large percentage of iron present, the material is found practically non-magnetic.

Photographic Map of the Normal Solar Spectrum (Second Series) made by Professor Rowland.—Exhibited by Mr. WILLIAM CROOKES, F.R.S., V.P.C.S.

Nine plates of the solar spectrum, wave-length 3270 to 6950. Each plate contains two strips, 3 feet long.

The spectrum has been projected from concave gratings, of six inches diameter and 21½ feet radius, ruled with 10,000 or 20,000 lines to the inch, giving definition hitherto undreamed of. The scale is placed within 1-20th Angström division, or 1-100,000th wave-length of its true position.

There are few instruments which will show more of the spectrum than can be found on this map, even below the line D, for the first line in B is shown widely triple. The original negative shows E, and even finer lines, like that at wave-lengths 5276·1 and 5914·3, plainly double. As to other maps of the spectrum made by measurement and drawing, it may be said that no comparison is possible. The photograph is the work of the sunlight itself, and the user of this map has the solar spectrum itself before him, and not a distorted drawing full of errors of wave-length and of intensity. The superiority is so great that there is no possibility of comparison.

In addition to the nine plates above described, there are exhibited two plates, each 2 ft. 10 ins. long, of the B

and D lines. The D lines are 3 inches apart, and the B group has an extent of about 24 inches.

Pitkin and Niblett's Fire-damp Meter.—Exhibited by Mr. James Pitkin.

By means of these instruments it is possible to detect and estimate the percentage of oxygen or hydrogen in mixtures of these gases.

In its simplest form it consists of two ordinary cylindrical bulbed mercurial thermometers. These are mounted on a suitable base, and are then graduated off in the ordinary way to the Fahr. or Cent. scale. One tube registers the temperature of the mixed gases. The other, which is the gas indicator, has its bulb coated with one of those metals which, when in a very finely divided state, have that peculiar property of occluding and facilitating the chemical combination of certain gases. When placed in a gaseous mixture, and during the combination of the gases due to the above property of the metal, a considerable amount of heat is developed. The heat generated thus produces a corresponding rise in the mercurial column. To read the instrument, the difference between the two-scale reading is taken, and then by comparison with a table supplied with each instrument, the percentage of gas may be read off.

In the case of fire-damp and air, or coal-gas and air, the amount of heat developed appears to correspond approximately to the explosive activity of the mixed gases. A sliding scale may be fixed on the instrument, which can be graduated in terms of percentages of any particular gas.

Combustion in Dried Oxygen.—Exhibited by Mr. H. Brereton Baker, M.A., Dulwich College.

(1). Charcoal is heated to redness in dried oxygen without any visible combustion. The oxygen has been in contact with the drying agent for two months.

(2). Sulphur is distilled in oxygen dried by phosphorus pentoxide for five years. No flame is seen. In moist oxygen sulphur burns at a temperature of 320°, its boiling-point is 440°.

(3). Phosphorus is distilled in oxygen dried in the same way. It boils at 290°. In moist oxygen it catches fire at about 60°.

(4). Ordinary phosphorus is not luminous at any pressure in dried oxygen. The tube on the right contains ordinary phosphorus in moist oxygen. If the corresponding mercury reservoir be lowered, the pressure in the tube will diminish, and the phosphorus will become luminous. The tube on the left contains phosphorus which has been carefully purified in oxygen which has been dried by contact with phosphorus pentoxide for four months. By lowering the mercury reservoir on the left, the pressure will be diminished in this tube, but no luminosity will appear. Phosphorus is thus proved not to undergo slow combustion in oxygen at a low pressure, if the oxygen be sufficiently dried. In these experiments the substances must not only be freed from moisture, but also from any traces of hydrogen, which, by its union with oxygen, would produce water. Before they are filled, the glass tubes are heated nearly to their melting-point, to free the glass from adhering moisture.

(5). Amorphous phosphorus is heated in a tube containing pure nitrogen in the vapour of boiling mercury (360°), without undergoing the change to the ordinary modification.

Amorphous phosphorus has been regarded as being incapable of undergoing true combustion. If heated to 260° in air or oxygen it burns, but it is generally supposed that this combustion is preceded by a change to ordinary phosphorus, which burns readily at this temperature. The experiment of heating the amorphous phosphorus in nitrogen proves that it does not change if it is heated in a neutral gas, and therefore that the combustion in oxygen is a true one, and is not necessarily preceded by a transformation to the ordinary modification.

An Experiment Showing an Effect of Light in Magnetising Iron.—Exhibited by Mr. Shelford Bidwell, M.A., F.R.S.

A bar of iron, which has undergone certain preliminary treatment, is placed close to a small reflecting magnetometer. When the iron is illuminated by an oxyhydrogen lamp, it instantly reflects the magnetometer needle, as is evidenced by the movement of the spot of light upon the scale; and when the illumination is cut off the spot of light at once goes back.

The preparation of the iron consists in first magnetising it by a current of electricity passed through a surrounding coil, and then very perfectly demagnetising it by a reversed current of suitable strength. Its magnetic condition is thus rendered unstable, and its susceptibility appears to be greater for a small magnetising force acting in the same direction as that by which the bar was at first magnetised, than for an equal small force in the opposite direction.

For further details see *Roy. Soc. Proc.*, vol xlv., p. 453, 1889.

Preparations of the New Element Gnomium, recently Discovered by Gerhard Krüss and F. W. Schmidt, of Munich.—Exhibited by Dr. Hugo Müller, F.R.S.

Gnomium oxide.

Gnomium chloride (in aqueous solution).

Nickel from which the Gnomium, which up to the present always accompanied it, has been separated.

Nickel oxide free from Gnomium.

Gnomium is a metallic metal which, according to the discovery of Krüss and Schmidt, is always associated with cobalt and nickel, and consequently neither of these metals have up to the present been known in the pure state.

Hollow Cylinder and Sphere, used in the Re-determination of the Weight of a Cubic-inch of Distilled Water, 1889.—Exhibited by Mr. H. J. Chaney.

t = 62°, B = 30 inches. One cubic inch = 252·286 grains.

Voltaic Balance.—Exhibited by Dr. G. Gore, F.R.S.

Used for measuring voltaic energy in chemical analysis; strength of aqueous solutions; detecting chemical changes in liquids and measuring their rates; detecting chemical compounds and their combining proportions; measuring losses of voltaic energy during chemical combination; measuring chemical energy.

By means of it the influence of 1 part by weight of chlorine in 500,000 million parts by weight of water has been detected.

Films of Metals and Metallic Oxides Deposited by Electric Sparks.—Exhibited by Prof. W. N. Hartley, F.R.S.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, May 6, 1889.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Vice-President, in the Chair.

The following Vice-Presidents for the ensuing year were announced:—

Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir James Crichton Browne, M.D., LL.D., F.R.S.; William Crookes, F.R.S.; Colonel James A. Grant, C.B., C.S.I., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; John Rae, M.D., LL.D., F.R.S.; Henry Pollock, Treasurer; Sir Frederick Bramwell, Bart. D.C.L., F.R.S., Hon. Secretary.

John Tyndall, D.C.L., LL.D., F.R.S., was elected Honorary Professor of Natural Philosophy.

The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S., was elected Professor of Natural Philosophy.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

CORRESPONDENCE.

ACETIC SULPHIDE.

To the Editor of the Chemical News.

Sir,—I have just found out that acetic sulphide, which I have never seen mentioned in books before, is obtained by distilling acetic chloride with trisulphide of antimony. Distilled with red oxide of lead, or red oxide of mercury, it yields acetic oxide. I also tried distilling glacial acetic acid saturated with sulphuretted hydrogen gas; but this did not seem to answer.

Acetic oxide is converted by hydrochloric acid into acetylchloride.—I am, &c.,

G. W. Blythe, M.P.S.

5, Alderley Road, Hoylake, Cheshire, May 2, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 7. April 5, 1889.

Notes on the Alkali Industry.— M. Scheurer-Kestner.—The author summarises the attempts which have recently been made at improving the known procedures and at creating novel ones. He notices in the first place Dr. Lunge's researches on the reactions which occur in the alkali manufacture on the Leblanc system, considered from a thermo-chemical point of view. He then examines the recovery of sulphur from tank-waste by the Chance process. Next he turns to consider Mr. W. W. Staveley's process for producing sodium carbonate from phenol and sodium sulphate, a proposal which, according to the calculations of the inventor, has little prospect of proving remunerative. Lastly, M. Scheurer-Kestner considers Messrs. Parnell and Simpson'e process for combining the Leblanc and the ammonia processes.

On a Nitrophenol "Campho-nitrophenol," an Isomer of Nitrocamphor-*a*.—P. Cazeneuve.—The compound obtained has a composition answering to the formula $C_{10}H_{15}(NO_2)O.H_2O$. It is white, more soluble in water than is camphoric acid, soluble in boiling water in all proportions, soluble in alcohol, ether, coloroform, and benzene.

On the Antiseptic Value of Campho-nitrophenol.—P. Cazeneuve.—According to the author's experiments the antiseptic powers of campho-nitrophenol is very feeble. It is poisonous to the higher animals only in very heavy doses.

On the Campho-nitrophenates.— P. Cazeneuve.—Campho-nitrophenol reddens litmus, decomposes carbonates, and forms readily salts, most of which are crystalline. The potassium, sodium, ammonium, copper, lead, zinc, iron, and barium salts are soluble in water. The salts of silver and mercury are sparingly soluble; those of lime, quinine, and cinchonine are insoluble.

Action of Maltose on Diastase during Saccharification.— L. Lindet.— The accumulation of maltose causes the arrest of saccharification; if the maltose disappears in the state of alcohol and carbonic acid, or of an insoluble phenylhydrazine compound, the diastase resumes its saccharifying activity.

Biedermann's Central-Blatt fur Agricultur Chemie.
Vol. xviii., Part 3.

Remarks on Hoar-Frost.—John Aitken.—This paper is credited to the "Naturwissenschaftliche Rundschau."

Analysis of Nile Water.—A. Muntz and M. Aubin.—From the *Comptes Rendus.*

The Relations of Atmospheric Nitrogen to Arable Soil.—Th. Schlösing.—From the *Comptes Rendus.*

The Detection of Nitrates in Soils.— M. Frank (*Landwirthschaftliche Jahrbücher*). — A controversy regarding the blue colouration of sand-granules by diphenylamine, which the former author seems to have referred to the presence of traces of nitrates, whilst Kreusler maintains that it is due to the presence of certain oxides of manganese and iron.

On the Humin-Compounds, their Origin and Properties.—F. Hoppe-Seyler (*Zeitschrift Phys. Chemie*).—In this memoir the author examines the formation of humin-substances in plants, the behaviour of cellulose and wood-gum, the composition and properties of tanninreds and phlobaphenes, the preparation and properties of the ulmine and humine compounds from carbohydrates, from phenols, from dead plants, and furfurol from the fusion of azulmic acid with caustic potash. The hymatomelanic acids of peat and lignite do not differ in their behaviour from those of the phlobaphenes.

Analysis of a Soil from the District of Washington.— E. A. Schneider.— From the *American Journal of Science.*

On the Assimilability of the Phosphoric Acid in Basic Slags.—Prof. Petermann (*Bulletin de la Station Agronomic de l'Etat à Gembloux*).—The conclusions arrived at are that finely-ground basic slag is an excellent manure. In experiments made with two kinds of spring-sown grain in a soil containing a sufficiency of the other ingredients of plant-food there was a rapid assimilation of the phosphoric acid present in the slag. The free lime in the slag remained inoperative, though the soils were poor in this constituent, containing only 2·37 and 1·53 parts per 1000. The considerable quantity of ferrous and ferric oxide in the slag was not found disadvantageous either for the prosperity of cereals or for the formation of starch in potatoes.

Experiments with Fish Guano.—Prof. Petermann.—About an equal number of diseased potatoes were found in plots manured with fish guano and in those where it was absent.—This fact is important, as controverting the prevalent opinion that organic manures favo ur the development of the dangerous *Peronospora.*

Manurial Experiments with Rice.— Prof. C. C. Georgeron.—From the *Bulletin of the Imperial College of Agriculture and Dendrology*, Tokio. A complete manure is recommended.

The Occurrence of Uric Acid in the Urine of Herbivora.—Franz Mittelbach.—The author detected uric acid in the urine of 23 oxen, 7 cows, 7 sheep, and a number of horses. It was not absent in any of the specimens examined. This result, if found general, will throw a new light on the comparative metabolism in the herbivora and in man.—*Zeitschrift Physiol. Chemie.*

Elementary Analysis of the Hæmoglobine of the Blood of Dogs.—Alfred Jacquet (*Zeitschrift Physiolog. Chemie*).—The hæmoglobines of the horse and the dog are not identical. That of the former contains less carbon, more nitrogen, less sulphur and iron, and more oxygen.

The Signification of Potash in the Plant.— R. Lupke (*Landwirthschaftlich. Jahrbucher*).—On experimenting on species of *Phaseolus* the author found that the presence of potash was not indispensable to the growth of the plants, though the plants fell short of their normal condition. What is the exact function of the potash, whether it is required for the chemical existence of the plant or if it subserves certain vital processes, are questions not yet solved.

Researches on the Nitrogenous Nutriment of Cereals and Legumens.—H. Hellriegel and H. Wilfarth (*Zeit. Rüben. Industrie*).

The Formation of Asparagine and the Relations of Non-nitrogenous Compounds to the Conversions of Albumen in the Vegetable Organism.—Prof. E. Schulze (*Landw. Jahrbücher*).

The Signification of Reserve-matter in Trees.—R. Hartig (*Botan. Zeitung*).

The Bacteria of the Tubers of the Papilionaceæ.—W. Beyerinck.—The last four memoirs do not admit of useful abstraction.

The Transformation of Potato Starch in the Human Stomach.—Dr. H. Zechnissen (*Centralblatt fur Medicin*).—In the human stomach, if empty, or with almost neutral or faintly acid contents, the dissolved starch is quickly converted into maltose and dextrine. After the previous ingestion of food the starch is never converted into sugar.

The Alsatian Method of Meadow-Culture.—N. N. (*Zeit. Spiritus Industrie*).—The land intended for irrigation is laid out in terraces.

The Ash of Coke as Manure.—N. Passerini (*Le Stazione Speriment. Agrar. Ital.*).—The ash of coke contains 5·7 per cent phosphoric anhydride and 0·53 of potash. A mixture of 700 parts coke-ash with 200 parts ammonium sulphate is recommended as a good manure.

Kainite as a Protection against Frost.—According to Heyking (*Sächsland Zeitung*) a top-dressing of kainite is said to have resisted a temperature of −7·5°.

Poisonous Character of Air Expired.—R. Würtz (*Central-blatt Medicine*).—The air expired was passed through a 1 per cent solution of oxalic acid, which is then neutralised with calcium carbonate and rendered alkaline with lime-water. The filtrate was neutralised with hydrochloric acid and evaporated in a vacuum and yields a mixture of hydrochlorates consisting chiefly of ammonium chloride. There was also present a base precipitable by mercury-potassium iodide, from which soluble salts of gold and platinum were obtained. The aqueous solution of the hydrochlorate has a peculiar aromatic odour.

The Occurrence of Fluorine in the Organism.—G. Tamman (*Zeit. Phys. Chemie*).—All organs rich in phosphorus contain ponderable quantities of fluorine, whence this element seems to play an important physiological part in the system.

MISCELLANEOUS.

Faraday Lecture.—Professor Mendeleeff's lecture will be on the Periodic Law of the Chemical Elements; it will be delivered in the theatre of the Royal Institution, Albemarle Street, W., on Tuesday, June 4th, at 8.30 p.m. Fellows requiring additional tickets for the Faraday Lecture are requested to apply to Mr. Hall. The tickets are available for ladies. The dinner at which the Fellows will entertain Professor Mendeleeff will take place at the Holborn Restaurant on Wednesday, June 5th, at 7 p.m. Tickets may be obtained from Mr. Hall, price half-a-guinea, not including wine.

Royal Institution.—The two following important donations have recently been made:—Mrs. de la Rue has presented to the Royal Institution the philosophical apparatus of the late Dr. Warren de la Rue; which will be preserved there as the historical collection commemorative of the important scientific work of Dr. Warren de la Rue, and of the eminent position he has so long occupied as a promoter of Science and of the special objects of the Institution; and a fine portrait of Sir Humphry Davy has been presented by Mr. James Young, grandson of the late Dr. James Young, F.R.S., of Kelly, the distinguished chemist, and former owner of the portrait, which makes a valuable addition to the collection of historic portraits now in the Royal Institution.

The Parkes Museum.—A General Meeting of this Society was held on Friday last, Dr. G. V. Poore in the chair, for the purpose of completing the arrangements necessary for carrying out the amalgamation of the Parkes Museum with the Sanitary Institute. Although the Parkes Museum will cease to exist as a separate body, it will still be carried on in the same premises as part of the Sanitary Institute, or combined Society, and its scope will be enlarged, and its usefulness greatly increased. In order to conform to legal technicalities it was necessary that it should be wound up, but it is satisfactory to note that the Parkes Museum in closing its works was able to transfer to the new Institute its Museum and Library, which has been a collection of many years, the lease of the premises, and also a cash balance amounting to nearly £900.

A Modification of the Kjeldahl Process.— Prof. J. W. Gunning.—The modification consists in adding to the acid employed a quantity of potassium sulphate. He uses a mixture obtained by melting together one part K_2SO_4 and two parts of ordinary acid. He remarks that there is scarcely any glass in commerce which does not give off noteworthy quantities of alkali if in contact with hot watery vapour in the act of condensation.—*Zeitschrift fur Analytische Chemie*, Vol. xxviii., Part 2.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Toughened Glass for the Laboratory.—Can glass retorts, &c., be purchased, which will only break by violence, but not by heat, or even sudden change of temperatures?—G. W. B.

Pigments.—Will any correspondent inform me which are the standard works in English, French, or German dealing practically with pigments and mixing colours?—B.

Fruit Essences.—I want a work on the best mode of producing artificial fruit essences and flavouring extracts (artificial). By supplying this information you will greatly oblige.—G. Newell, M.D.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.

Tuesday, 21st.—Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.

Wednesday, 22nd.—Geological, 8.
—— Society of Arts, 8. (Ordinary Meeting). "The Use of Spirit as an Agent in Prime Movers," by A. F. Yarrow.

Thursday, 23rd.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Chemical Affinity," by Professor Dewar.

Friday, 24th.—Quekett Club, 8.
—— Royal Institution, 9. "The Solar Surface during the Last Ten Years," by the Rev. S. J. Perry.

Saturday, 25th.—Royal Institution, 3. "The Origin and Development of Opera in England," by Joseph Bennett.
—— Physical, 3. "On a Relation existing between the Density and Refraction of the Gaseous Elements and some of their Compounds," by the Rev. T. Pelham Dale. "On a Waterspray Influence Machine," by Mr. George Fuller. "Notes on Polarised Light—(*a*) On the Transition Tints of Various Orders, (*b*) Lecture Illustrations of the Rotation of the Plane of Polarisation, (*c*) On the Rotation of Circularly Polarised and non-polarised Light," by Prof. S. P. Thompson, D.Sc. "Terrestrial Magnetism as Modified by the Structure of the Earth's Crust," by Dr. Edmund Naumann. "On the Molecular Weight of Caoutchouc and other Colloric Bodies," by Dr. J. H. Gladstone and Mr. W. Hibbert.

Analytical Chemist Wanted.—One preferred who has been accustomed to examine Oil and Grease. State experience and salary expected.—Address No. 444, CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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Dated this 8th day of May, 1889.

By Order,
EDWARD CROWNE.
Clerk to the Board.

Local Board Office,
Tottenham, N.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that MAURICE BAUER, of 8, Union Court, in the City of London, has applied for leave to amend the Specification of Letters Patent No. 9352 of 1885, for "Improvements in extracting fat and other substances from dissolvable materials and in apparatus therefor."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 8th May, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)
H. READER LACK,
Comptroller-General.

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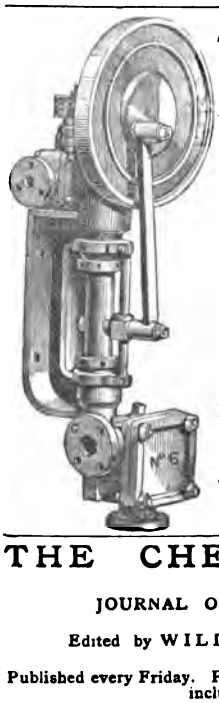

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BOY COURT, LUDGATE HILL, LONDON, E.C.

THE CHEMICAL NEWS.

VOL. LIX. No. 1539.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,
Professor of Chemistry in the University of Virginia.

AFTER noticing and giving the results of the earlier determinations of the atomic weight of gold, and the recent researches of Krüss and of Thorpe and Laurie, the author reports upon experiments of his own in the same direction, which have occupied much of his time and labour for the last three or four years.

The difficulties connected with the accurate determination of the atomic weight of this metal are remarked upon, and the general principles are reviewed which ought to be observed in all investigations of this kind.

The means and methods of weighing used are stated, and the precautions are described in detail which were resorted to in purifying the metallic gold to be employed in the research, with the history of some samples of "proof" and "trial plate" gold, obtained from the Mint establishments of the United States and England. The general precautions observed in the course of the work are described, particularly the use of an arrangement for evaporating some of the gold solutions with exclusion of the organic matter of atmospheric dust.

A detailed account is given of the methods adopted in seven series of experiments, looking to more or less independent determinations of the atomic weight sought, viz. :—

First Series.—Division of a uniform, neutral solution in water, of auric chloride into two accurately weighed and nearly equal portions; precipitation from the one portion by sulphur dioxide of metallic gold, which was collected and weighed; determination, with special precautions, of the quantity of metallic silver required as nitrate to precipitate the chlorine in the other portion.

Second Series.—Similar treatment of a neutral solution of auric bromide, giving the quantity of gold in one portion and the quantity of silver required to precipitate bromine in the other portion.

Third Series.—Similar treatment of a solution of repeatedly crystallised potassium auri-bromide, again giving the quantity of gold in one portion, and the silver equivalent to the whole of the bromine in the other portion.

Fourth Series.—Determination of the loss by ignition of a weighed quantity of trimethyl-ammonium auri-chloride.

Fifth Series.—Comparison of the weights of gold and silver simultaneously deposited by the same electric current from aqueous solutions of auro-cyanide and argento-cyanide of potassium respectively.

Sixth Series.—Comparison of the weight of gold deposited from a solution of potassium auro-cyanide on electrolysis with the volume of hydrogen liberated by the same current from dilute sulphuric acid, the hydrogen evolved in a voltameter of special construction, and measured of course under well-defined conditions of temperature and pressure.

Seventh Series.—Determination of the volume of hydrogen, under known conditions of temperature and pressure, obtainable by solution in dilute sulphuric acid of a given quantity of specially purified metallic zinc; use of a definite quantity of the same zinc, taken in small excess, to precipitate gold from a neutral solution of auric chloride, and determination of the quantity of metallic gold thrown down; determination of the volume of hydrogen obtainable on solution in dilute sulphuric acid of the *excess* of zinc thus used. Resulting comparison of the quantity of gold in solution as auric chloride with the quantity of hydrogen equivalent to the metal.

The results obtained are thus stated as follows:—

		Atomic weight of gold.		
		Average value from aggregate weights.	Lowest value from a single experiment.	Highest value from a single experiment.
1st series (5 experiments)	..	196·722	196·688	196·770
2nd ,, (6 ,,)	..	196·790	196·731	196·843
3rd ,, (4 ,,)	..	196·775	196·685	196·817
4th ,, (5 ,,)	..	197·225	197·131	197·289
5th ,, (5 ,,)	..	196·823	196·709	196·945
6th ,, (3 ,,)	..	197·137	196·994	197·283
7th ,, (6 ,,)	..	196·897	196·848	196·956

If the general mean be taken of the results of all these series of experiments, using the average value derived from each, and giving all an equal weight, the number 196·910 is obtained for the atomic weight of gold.

But reasons are given for feeling much less confidence in the results of the fifth and sixth series of experiments (made by electrolysis) than in the rest; if these two series be excluded the general mean becomes 196·882.

A certain degree of suspicion as to possible constant error having been shown to perhaps affect the results of the fourth series if this also be left out, and only the firs three and the seventh series be considered, the general mean will be 196·796.

And finally, if, for the sake of comparison with the results of the recent researches of other chemists, only the first three series be included, in which auric chloride and bromide were examined, the general mean will be 196·762—a result rather higher than that of Krüss and lower than that of Thorpe and Laurie, but nearer to the latter than the former.

In conclusion, reference is made to the bearing of the results reached on Mendeleeff's periodic classification of the elements, and on the hypothesis of Prout, and attention is drawn to the desirability of a general re-examination of atomic weights, not by a single method only in each case, or by methods more or less nearly similar or dependent on each other, resting satisfied with a close agreement of results under these conditions, but by as many distinct and independent methods as may be possible for each element examined.

* Abstract of a Paper read before the Royal Society, May 9, 1889.

DETERMINING THE STRENGTH OF LIQUIDS BY MEANS OF THE VOLTAIC BALANCE.*

By Dr. G. GORE, F.R.S.

THIS method is based upon the circumstance that the greater the degree of concentration of a solution, the larger is the amount of dilution required to reduce its voltaic energy to a given magnitude.

In a research on the "Relative Amounts of Voltaic Energy of Electrolytes (*Roy. Soc. Proc*, vol. xlv., p. 268), I have described the method of measuring the voltaic energy of a substance, and have given the magnitudes of such energy excited in a voltaic couple of unamalgamated zinc and platinum by upwards of one hundred different substances when dissolved in water, in relation to that excited in the same couple by water alone, all the liquids being at the atmospheric temperature.

* Read before the Royal Society, May 9, 1889.

In the present research, as examples of the applicability of the voltaic balance to determine the degree of concentration of liquids, I have taken aqueous solutions of nitric acid, hydrochloric acid, sulphuric acid, common salt, ammonia, and carbonate of soda, and ascertained the degree of strength of each by chemical analysis, by specific gravity, and by the voltaic balance method. The following numbers represent the proportions of water which were required by one part by weight of each of these substances, in order to reduce its voltaic energy to the same magnitude, viz., to that required to just visibly move the needles of the galvanometer, and they therefore also represent the relative magnitudes of voltaic energy of the substances indicated by the respective formulæ.

	Between—		Temp. °C.	Average energy.
HCl ..	9,300,000	and 9,388,185	at 16·5 ..	9,344,092
H_2SO_4 .	3,690,476	,, 4,111,446	at 19 ..	3,900,941
HNO_3..	3,039,215	,, 3,369,565	at 19 ..	3,204,395
NaCl ..	190,570	,, 221,428	at 15 ..	207,589
Na_2CO_3	−14,090	,, −15,550	at 19 ..	−14,795
H_3N ..	−281,818	,, −313,765	at 15 ..	−297,791

In each example given a known volume of solution was taken, and the proportion of substance in it was found by ordinary chemical analysis. A second portion was taken, its specific gravity ascertained by the method of weighing, and its degree of strength found by aid of the ordinary published tables of specific gravity. A third portion of known volume was then taken, its average amount of voltaic energy measured, and its degree of concentration found by the amount of dilution required to reduce its energy to the same magnitude; the less dilute it was at starting the greater the amount of dilution required. The following are the results:—

By—	HCl.	H_2SO_4.	HNO_3.	NaCl.	Na_2CO_3.	H_3N
Chemical analysis..	1·85	5·60	2·97	9·13	7·21	1·05
Specific gravity ..	1·70	5·44	2·80	8·74	7·63	1·03
Voltaic balance ..	1·65	5·70	2·90	8·71	7·57	1·06

The variations in the numbers are partly due to inequalities of temperature.

A much less quantity of substance is usually required by the voltaic balance than by either of the other methods, and the operation is quickly and easily performed.

INDIGO STEM ASH.

By JOHN TSAWOO WHITE.

It may not be uninteresting to record an unpublished complete analysis of the ash of the indigo stem (*Indigofera tinctoria*), an analysis which I finished some three years ago, in the laboratory of the Chemical Examiner to Government, Burma, at a time when I was engaged in some plant-ash determinations.

	I.	II.
Charcoal	4·76	—
Sand	9·99	—
CO_2	8·95	10·56
SiO_2	7·21	8·51
SO_3	5·31	6·27
Fe_2O_3	4·58	5·41
P_2O_5	10·37	12·24
CaO	16·40	19·36
MgO	9·86	11·64
K_2O	16·12	19·03
Na_2O	4·00	4·72
NaCl	1·91	2·26
	99·46	100·00

The sample analysed was grown on the Government Experimental Farm at Alôn, under the charge of Dr. R. Romanis, the Chemical Examiner. Some manuring experiments were tried with nitre and with potassium chloride. The potassium chloride produced no effect, while the nitre is said to make the plants more vigorous.

The ash was prepared by heating the dry stem, after peeling off the bark, on a large sheet of platinum-foil over an argand flame at as low a temperature as possible. The grey ash was weighed, powdered, and put into a stoppered bottle. 1614 grms. of the stem gave 29·4 grms. of ash, equal to 1·8 per cent. The ash determination is given below. The analysis was conducted according to Fresenius.

The numbers in column II. are obtained from those in I. by cancelling charcoal and sand, which are regarded as unessential, and calculating the percentage of the rest. The numbers must be allowed to speak for themselves.

Sand and silica were separated by a strong solution of sodium carbonate in a nickel basin. At first I did not intend to try this separation, but after igniting and weighing the sand and silica together, I thought that I might try its solubility in sodium carbonate. The soluble portion was noted down as silica, and the insoluble matter was called sand. The separation may be imperfect. Will sodium carbonate solution effectually separate silica from sand even after ignition? The potassium oxide was obtained from the weight of its platinichloride.

It was intended to try the composition of the ash of the leaves as well, but the resolution was never carried out.

Rangoon College,
March 28, 1889.

ON THE ATOMIC WEIGHT OF OXYGEN.

By W. A. NOYES.

The great importance which attaches to the atomic weight of oxygen makes it very desirable that this constant should be determined by several methods and by independent workers.

The method to be described was suggested to the author of this paper when reading Keiser's first paper.* A somewhat similar method has been proposed for a different purpose by Morley.†

The results which I have thus far obtained I consider as only preliminary, and they are presented now because it is necessary to discontinue the work for some time, and because they may be of some interest to others who are working in the same field.

The fundamental idea of the method is that by passing hydrogen into an apparatus containing hot copper oxide, and condensing the water formed within the same apparatus, the weight of the hydrogen can be determined by the gain in weight of the apparatus. The form of apparatus which was found best suited for the purpose is illustrated in the accompanying cut. It was made by Emil Greiner in New York.

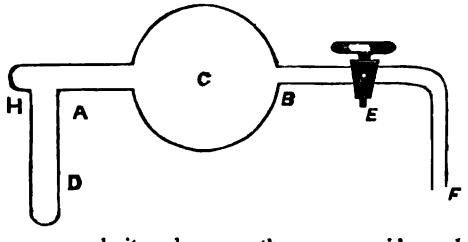
C is a bulb with a capacity of 30 to 50 c.c. and will contain 90 to 150 grms. of copper oxide. The tube H was open when the apparatus was received from the maker. A small plug of asbestos was first placed at B, the bulb C was filled with carefully ignited copper oxide (Kahlbaum's best in wire form), and the tube was sealed at H. The volume of the apparatus was then determined by weighing in air and in water, and a counterpoise of nearly the same volume and of somewhat less weight was prepared. The tube F was then connected with a Sprengel pump by means of a bulb containing phosphorus pentoxide, and the air was pumped out. During the exhaustion the bulb was heated in an appropriate air-bath. After exhaustion, the apparatus was allowed to cool and was then weighed,

* *Ber. d. chem. Ges.*, xx, 2323.
† *American Chemical Journal*, x., 22.

using the counterpoise before mentioned. The balance used was made by Ruprecht in Vienna, and the weight of the apparatus (150 to 220 grms.) could easily be determined to $\frac{1}{10}$ m.grm. The apparatus was always allowed to stand in the closed balance-case for several hours, and usually over night, before the weight was finally determined. The volume of the counterpoise and weights was the same as that of the apparatus, within 1·5 c.c. in every case, and usually somewhat closer. The greatest difference of temperature between the two weighings which gave the hydrogen was four degrees, and the greatest difference in pressure was seven m.m. Supposing the differences to have occurred at the same time and in the same direction, and the difference in volume to have been 1·5 c.c., the error from this source would have been four one-hundredths of a m.grm.

No correction to vacuum was necessary, as all of the weights for a determination were made with an apparatus of the same volume, and were determined with weights whose relative values had been determined by calibration *in the air*.

After weighing, the apparatus was again placed in the air-bath and heated while it was connected with an apparatus giving carefully purified hydrogen. The connection at F was sometimes made with a short piece of rubber tubing, the two tubes being brought together within it and the whole covered with mercury to prevent possible leakage or diffusion, and sometimes by a ground glass joint lubricated with a little grease. Each method seemed to serve equally well, except in one case, when a little mercury was drawn in through the rubber joint. In that case a low result was obtained, probably because of the vapour of mercury taken up by the hydrogen. When the hydrogen is first admitted to the apparatus through the



three-way cock, it rushes over the copper oxide, and only a part of it is converted into water. Very soon a condition is reached when the side-tube D is filled with hydrogen, while the bulb is filled with nearly pure water-vapour. The hydrogen slowly diffuses back to the copper oxide, where it is converted into water-vapour, while the water-vapour diffuses into D and is condensed. The tube A and the opening into D are made about one c.m. in diameter, that the diffusion may be as rapid as possible. D is cooled by immersion into distilled water. From two to four litres of hydrogen can be passed into the apparatus and converted into water in an hour. In a part of the experiments, the results of which are given below, a U-tube was used in place of the bulb to contain the copper oxide, but that form of apparatus was found less suitable.

After passing in a suitable amount of hydrogen, the stop-cock was closed, and by continuing the heating for a short time, all of the *gaseous* hydrogen was converted into water. The apparatus was then cooled and weighed with the same precautions as at first. The apparatus was then connected with a Sprengel pump by means of a bulb surrounded with ice-water. After exhausting the bulb and the tube F, the stop-cock was turned, and the small amount of nitrogen which always remained in the apparatus was pumped out and delivered into a eudiometer, where it was measured and further examined. Meanwhile the tube was heated in the air-bath, and the tube D was surrounded with hot water. As the water in D had been for several hours in an almost perfect vacuum, the water on the outside could be heated to boiling without fear of any ebullition within the tube. The water evaporated quite rapidly from the surface, and 6 or 8 c.c. could be expelled from the apparatus in about an hour. In some of the experiments the apparatus was then connected with a vacuous bulb filled with phosphorus pentoxide, while in others it was cooled and weighed without this step. The vapour remaining in the apparatus in the latter case was very small in amount, and was determined along with the water obtained by re-oxidising the reduced copper. After cooling and weighing, the apparatus was again placed in the air-bath and heated, and oxygen from a gasometer was passed in. The oxygen was passed over heated copper oxide, through a strong solution of caustic potash, and over stick potash and phosphorus pentoxide.

At this point arose one of the most serious questions with regard to the process. It was found that, even after very prolonged heating in pure oxygen, the copper would not take up as much oxygen as had been taken from it by the hydrogen. The explanation seems to be that the hydrogen, as it reduces the copper oxide, leaves the copper in a porous condition, so that the last traces of oxygen can be taken from it by the hydrogen. When the oxygen is passed in, however, the copper on the surface is oxidised first and the copper oxide formed, filling a greater volume than the copper; the pores are almost or quite closed, and the copper within is protected from further oxidation. Whether the copper loses all of the hydrogen which it has absorbed, as Keiser has shown that palladium does, is, perhaps, a question. The only direct evidence which has been thus far obtained on this point was one case in which the copper was heated twice in an atmosphere of oxygen. On the first heating it absorbed two grms. of oxygen and gave 0·0160 grm. water. On the second heating the copper absorbed one-half grm. of oxygen and gave only 0·0013 grm. water. The heating in the second case was continued for two hours. In other cases the heating was continued much longer, and the re-oxidation was still far from complete. Even in some cases when copper reduced in hydrogen and re-oxidised in oxygen was used, the copper could not, after a second reduction, be made to take up the same amount of oxygen again. If the copper remaining unoxidised still retained hydrogen, it would seem that the determinations of Cooke and Keiser must have been subject to an error from the same source. Such an error must have been very small, but it is desirable that some determinations should be made by means of another agent than copper oxide.

After passing in the oxygen, the apparatus was cooled and weighed. It was then heated again, and the gases remaining in it pumped out into a eudiometer, while the water formed was received in a bulb filled with phosphorus pentoxide. On cooling and weighing, the loss of weight, less the weight of the gases pumped out, as determined by analysis, gave the weight of water obtained from the hydrogen which had been absorbed by the copper. Errors in any of these last weights would have only one-ninth as great an effect on the result as errors in the weights by which the amount of the hydrogen was determined. The amount of the water obtained after the oxidation of the copper was quite variable, partly because in some cases the bulb was only connected with the vacuous bulb surrounded with ice-water before re-oxidation and so remained filled with aqueous vapour at a very low tension, and partly because the copper oxide used had been reduced and only partly re-oxidised as stated above, and in such cases the amount of metallic copper was much greater in proportion to the amount of water first formed than in other cases.

The hydrogen was prepared from pure (?) zinc and pure hydrochloric acid. The latter was of specific gravity 1·12, and was boiled carefully and partly cooled in a current of hydrogen before it was introduced into the flask from which it was fed to the generator. Also, pieces of

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Per cent of oxygen re-absorbed.	Atomic Weight.
1.	0·9449	7·4785	0·0006	0·0215	0·9443	7·4976	31	15·880
2.	0·6760	5·3521	0·0016	0·0034	0·6744	5·3551	28	15·881
3.	0·7879	6·2432	0·0013	0·0137	0·7866	6·2554	43	15·905
4.	0·5527	4·3483	0·0006	0·0420	0·5521	4·3856	61	15·887
5.	0·4278	3·3366	0·0004	0·0631	0·4274	3·3927	65	15·876
6.	0·8271	6·5437	0·0006	0·0249	0·8265	6·5658	27	15·888

Mean = 15·886 ± 0·0028

pure zinc were put into it, to more thoroughly wash out dissolved gases and to furnish nascent hydrogen which should remove the last traces of oxygen from the liquid. Contact with the air was carefully avoided, and the acid was fed into the generator from a flask filled above with hydrogen, either by an arrangement similar to that described by Cooke, or with hydrogen from an independent generator. After the introduction of the hydrochloric acid into the feed-flask, a solution of blue chromous chloride was added. This was obtained by the reduction of potassium pyrochromate with zinc and hydrochloric acid. Its purpose was to absorb any traces of oxygen, and to give evidence of any air in the apparatus, by its change in colour. The heavy flask used for a generator had a capacity of one litre, and had but one neck. The rubber stopper, bearing four tubes, was sunk into the neck, and covered with a thin layer of mercury, to prevent possible diffusion. The acid was fed by a syphon, and only its vapour came in contact with the stoppers. When hydrogen from the generator was used in the feed-flask, the stopper of the latter was surrounded with a jacket filled with mercury.

From the generator the hydrogen was passed through a 20-bulb tube filled with a 30 per cent solution of caustic potash, to which some lead chloride was added. The latter revealed the presence of a small amount of hydrogen sulphide. Next was an 8-bulb tube containing a 3 per cent solution of potassium permanganate, then a layer of hot copper. This was omitted in the first determinations, and was introduced from fear of a trace of oxygen from the potassium permanganate. After its introduction, a trace of hydrogen sulphide was found in the strong caustic potash solution which followed. This may have come from the rubber joints at both ends of the tube containing the copper. These joints could not be sealed, as they were between hard and soft glass. The joint at the other end of the potassium permanganate tube was also of rubber, because the solution required frequent renewal. The tubes were brought close together within these joints, and they were covered with jackets filled with water, to prevent diffusion. All other joints were made by fusing the glass together. After the copper, the hydrogen passed a strong caustic potash solution, to which lead sulphate was added in the later experiments, and then over stick potash and over phosphorus pentoxide mixed with asbestos. Glass-wool was avoided, because a specimen examined was found to have so low a specific gravity as to prove that it consisted—in part, at least—of fine glass tubes, and it was feared that the air in these would diffuse out slowly and mix with the hydrogen. After passing the phosphorus pentoxide an overflow tube was provided, dipping under mercury.

In calculating the results, the weight of the hydrogen, determined by the gain in weight of the apparatus, was corrected by subtracting the weight of the gas which was obtained in removing the water formed, as described above. This gas was calculated as nitrogen. In every case but one, however, oxygen was added in excess, then hydrogen, and the mixture was exploded. The results would seem to indicate that the gas contained from six to eleven thousandths of a m.grm. of hydrogen, but it is believed that this apparent result came from the formation of a small amount of oxides of nitrogen by the explosion. The oxygen was determined by the loss in weight of the apparatus after the water was removed. To this was added eight-ninths of the weight of the water obtained by re-oxidising the copper.

Two determinations are omitted in the results given below. In one of these, mercury leaked by the rubber joint, and some of its vapour probably entered with the hydrogen. In the other, a small amount only of the hydrogen was used, and the accidental error was probably large. The other determinations were as in Table above.

It is of especial interest to compare this result with that obtained by Cooke, who prepared his hydrogen from the same materials. His result was 15·869, and the probable error of his first series is one-half greater than that of this series, while that of his second series is but little less than this. *If the correction for nitrogen is omitted, the mean of these determinations becomes* 15·867, *or almost exactly the same as Cooke's final mean.* It seems to the author that the evidence is almost conclusive that Cooke's hydrogen was contaminated with a trace of nitrogen. While the amount of nitrogen can be rendered very small (in one case less than ½ c.c. in 10½ litres), it would seem to be impossible to entirely exclude it with such generators as Cooke and myself have used.

In this series, the apparatus for purifying the hydrogen and also the condition of the copper oxide was repeatedly varied, in the endeavour to discover sources of constant error. One determination has also been made, using dilute sulphuric acid instead of hydrochloric. The result was 15·874.

The results obtained show that the accidental errors of the determination have been made very small. When the result is compared with that obtained by Keiser, however, I am inclined to believe that there must be in these determinations, as well as in those of Cooke, some source of constant error which has not yet been discovered.—*American Chemical Journal*, Vol., ii., No. 3.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, May 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II, the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, the whole were found to be clear, bright, and well filtered.

The quality of the water supply has continued throughout the month to be entirely satisfactory. Its composition has not been found to differ to any noteworthy extent from that observed to prevail during the first three months of the year; but the slight variation that has been recognised is in the direction of an increased degree of freedom from organic matter. Thus, in the case of the Thames-derived samples examined during the month, the mean proportion of organic carbon was found to be 0·154 part in 100,000 parts of the water, as against a mean of 0·164 part furnished by the previous three months' supply. The maximum proportion of organic carbon met with in any single sample of Thames-derived water examined during the month was found to be 0·170 part in 100,000 parts of the water. The difference in mean composition of the Thames-derived water, as supplied by the different companies, was, as usual, wholly insignificant. This, our hundredth monthly report, completes the record of the results of our examination of over 18,000 samples of the water supply of the Metropolis.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. C. Heinrich Trinks and Ernest F. Ehrhardt were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William D. Cargill, B.Sc., Longbaugh, near Dundee; Henry W. Morrow, B.S., Wilmington, Delaware, U.S.A.; and Robert Redwood, 85, Gracechurch Street, E.C.

The following were elected Fellows of the Society:—William Taylor Gibbs, Byron B. Goldsmith, Charles James Grist, John Kitchin, John Edmund Legg, Francis Ransom, Alfred Edward Sibson, Ignatius Singer, Walter J. Sykes, and William Virtue.

The following papers were read:—

47. "*The Magnetic Rotation of Nitrogen Compounds.*" By W. H. Perkin, Ph.D., F.R.S.

In previous communications the author has shown that in the magnetic field the plane of polarisation of light is rotated to a greater extent in unsaturated than in saturated carbon compounds; in the present communication it is shown that in the case of nitrogen compounds the magnetic rotation is in like manner correlated with changes in the valency of the nitrogen.

Nitrates, Nitrites, and Nitro-compounds.—The specific rotation of all these is low, thus—

Nitric acid	1·180
Methylic nitrate	2·057
Ethylic „	3·084
Propylic „	4·085
Isobutylic „	5·180
Ethylenic „	3·768
Glyceric „ (nitro-glycerin	5·405
Isobutylic nitrite	5·510
Nitromethane	1·858
Nitroethane	2·837
Chloropicrin	5·384

The change attending the conversion of nitric acid into an ethereal salt is comparable with that of the acids of the acetic series into ethereal salts, the increase in the value for the nitrate being less than may be expected from the change in composition, thus—

Methylic nitrate	2·057
Nitric acid	1·180
	0·877
Methylic formate	2·495
Formic acid	1·671
	0·824
Usual value of CH_2	1·023

The high rotation of isobutylic nitrite in comparison with that of the corresponding nitrate is an illustration of the influence exercised by unsaturated nitrogen; it is also noteworthy that the rotation of chloropicrin is less than that of chloroform (5·559).

Amines.—Very nearly the same value is obtained for ammonia, whether aqueous or alcoholic solutions be taken, the former giving 1·81, the latter 1·826; the aqueous solution examined contained 31 per cent, the alcoholic 14·48 per cent NH_3: hence it would appear that little, if any, combination takes place between the ammonia and the solvent. Similar observations made with mixtures of equal volumes of isobutylamine and water or alcohol, and with a mixture of piperidine and water in the proportions $C_5H_{11}N : OH_2$, indicate, however, that combination takes place to some extent in these cases, the found and calculated values being as follows:—

	Calculated.	Found.	Difference.
Isobutylamine and water	11·200	11·099	0·101
„ „ alcohol	10·459	10·361	0·098
Piperidine and water	6·810	6·724	0·086

The effect of hydrocarbon radicles on amines was studied in the following cases:—

Ethylamine	3·609
Diethylamine	5·662
Triethylamine	8·518
Propylamine	4·563
Dipropylamine	7·549
Tripropylamine	11·664
Isobutylamine	5·692
Diisobutylamine	9·936
Allylamine	5·587
Pentamethylenediamine	7·491
Aniline	16·162
Methylaniline	19·629
Dimethylaniline	22·823
Piperidine	5·810
Pyridine	8·761

From these numbers it will be seen that the effect of introducing a single radicle into ammonia is somewhat less than corresponds to a similar change in homologous series, viz., 1·023 per CH_2. The rotation is increased proportionally more by the displacement of a second hydrogen atom, and in the paraffinoid amines a very remarkable increase attends the introduction of the third radicle, indicating a marked difference to exist between secondary and tertiary amines. The effect of methyl in aniline is also very remarkable, the increase in the rotation being more than three times that which usually follows such an alteration in empirical composition in paraffinoid compounds. The value for piperidine is very

low, and is in accordance with the conclusion that it is a saturated compound; the value for pyridine is also low in comparison with aniline and benzene (11·297).

The study of the salts of the amines has afforded noteworthy results: instead of the diminution which usually attends the formation of compounds, it is found that the observed rotation is slightly in excess of that calculated by adding the rotations of the constituent compounds in the case of the following ammonium chlorides:—

	Found.	Calc.	Diff.
Ammonium chloride	6·096	6·032	+0·064
Ethylammonium chloride ..	7·997	7·823	+0·174
Diethylammonium chloride	9·896	9·876	+0·020
Piperidinium chloride	10·034	10·024	+0·010

Triethylamine, however, behaves "normally," and a normal result is also obtained in the case of ammonium nitrate and sulphate, thus—

	Found.	Calc.	Diff.
Triethylammonium chloride	11·724	12·732	−1·008
Ammonium nitrate	2·316	2·998	−0·686
,, sulphate	4·963	5·951	−0·988

From the discussion of his results generally, the author arrives at the conclusion that in compounds of unsaturated "triad" nitrogen, the nitrogen has a greater influence than when it is present in the saturated condition, the difference in the values being about 0·5; this is only about half the difference usually observed on comparing the rotations of carbon compounds differing by 2H.

Discussion.

Dr. Gladstone said that the general result of Dr. Perkin's work, establishing a difference in nitrogen according as it is present in the saturated or unsaturated condition, was in accordance with the conclusion which he had arrived at from the study of refractive power; the peculiarities brought out by the study of the magnetic behaviour, however, were chiefly indicated by peculiarities in dispersive power, being less obvious in the refraction equivalents.

Professor Ramsay said that he should like, on some future occasion, to raise a discussion on the method adopted by Dr. Perkin and Dr. Gladstone in dealing with their results. He thought that the method followed by Schroeder in discussing volume constitution was perhaps applicable, and, at all events, deserving of attention.

48. "*The Nature of Solutions, as Elucidated by a Study of their Densities, Electric Conductivities, Heat Capacity, and Heat of Dissolution.*" By S. U. Pickering.

The solutions which form the subjects of this research are those of calcium chloride, calcium nitrate, and sulphuric acid. The results obtained with the first of these have already been brought before the Society (*Chem. Soc. Proc.*, 1888, 35), and tended to show that the curves representing the densities and heat of dissolution, of solutions of different strengths, though apparently regular on a superficial inspection, are not really so; when they are analysed by differentiation they are resolved into a series of curves or straight lines, showing that breaks occur in the original curves; these breaks, moreover, correspond to hydrates of definite composition. The densities gave a series of straight lines on the first differentiation, bearing out Mendeleeff's statement that such was the nature of the density curves in the case of sulphuric acid and alcohol, whereas the heat of dissolution required two differentiations before it gave straight lines.

With calcium nitrate the determinations which have been made are much more numerous, and the results obtained are of a nature precisely similar to those with calcium chloride. The straight lines formed by the first differential coefficient of the densities are in this case inclined to each other so very slightly, as scarcely to warrant the conclusion that the whole figure is not a continuous curve, were it not that the heat results confirm in every detail the breaks which the rectilineal drawing of the density differential shows. The heat capacities (specific heat) of very weak solutions of this salt have also been determined, and they are found to afford a rectilineal figure, indicating breaks at the same points as those deduced from the density and heat results.

The author has proceeded to an extensive examination of sulphuric acid solutions. On plotting out the first differential of his density results, he was surprised to find that it formed an irregularly curved figure, and not the rectilineal figure given by Mendeleeff, and he was still more surprised to find that on plotting out the values used by Mendeleeff himself, the figure obtained was curvilinear, like his own, and not rectilinear, like Mendeleeff's. This led him to plot out Mendeleeff's values for the first differential of the densities of alcohol, and in this case also he found that they gave an irregular curve, and not the rectilineal figure depicted by Mendeleeff in the *Journal* (*Trans.*, 1887, 780). Mendeleeff's statement, therefore, that he had proved the hydrate theory by showing that the densities differentiated into straight lines meeting at points corresponding to definite hydrates, is erroneous.

On applying a second differentiation to his density results with sulphuric acid the author obtained a series of straight lines, so that the density curve in this case resembles the heat curves in the case of the two calcium salts, and it is probable that the densities of these latter salts give rectilineal figures on the first differentiation only, because the constituent lines are straight within experimental error, and not because they are straight in reality.

The author has made determinations with a series of sulphuric acid solutions at four different temperatures, 8°, 18°, 28°, and 38°. The results obtained and the breaks shown were the same in every case, and the latter were found to become more apparent as the temperature is lower. The same conclusions as to the effect of a lowering of temperature in intensifying the change in general direction of the curve may be drawn from Mendeleeff's determinations with alcohol at different temperatures.

Crompton's interpretation of Kohlrausch's determination of the electric conductivity of sulphuric acid solutions is next discussed. The author agrees with Crompton's conclusion that they give a rectilineal figure after two differentiations, but he differs from him in some of the details as to where the breaks occur, and shows that the most probable position of these breaks agree very closely with those shown by his own density results.

The heat capacity of sulphuric acid solutions up to a strength of 12 per cent was next determined, and the results were found to form a series of very slightly curved lines, indicating breaks very clearly at the same points as did the densities. The original curves probably require two differentiations before they are reduced to straight lines.

The determination of the heat of dissolution of sulphuric acid solutions with the requisite degree of accuracy presented considerable difficulties, owing to the large amount of heat evolved. The results obtained confirmed the author's conclusions as to the nature of the heat curves in the case of the calcium salts. The whole curve was found to be made up of a series of independent curves, each of which gave a straight line on two, or sometimes on one differentiation, and the breaks agree in position with those deduced from the other properties. Although Thomsen's determinations of the heat of dissolution of sulphuric acid are far too few in number to prove the real nature of the curve, the author shows that they are quite sufficient to disprove the perfect regularity which Thomsen and his followers attribute to the interaction. Some marked changes are shown by it, and Thomsen's equation, which is supposed to represent the curve so faithfully, is applicable, in reality, to but 1 per cent of the whole figure.

The various hydrates which are proved by this work to

exist in solution are numerous and complex. Those which calcium chloride forms contain 6, 7, 8, 10, 13, 18, 28, 86, and 1500 H_2O; calcium nitrate gives hydrates with 3, 3·5, 4·5, 5, 6, 10, 17, 51, 265, and 1810 H_2O; while with sulphuric acid we find hydrates with $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, 1, $\frac{3}{4}$, 2, 4, 5, 9, 13, 24, 52, 135, 510, 1430, and 4950 H_2O. The existence of these is, naturally, more doubtful in some cases than in others, and it is impossible to determine the exact molecular composition when more than about 10 H_2O is present. In some cases the hydrates of sulphuric acid have been established by six independent sets of results obtained from the study of four distinct properties.

The excessively large amount of water present in the highest hydrate is a matter of especial interest, and the existence of such compounds explains the influence which mere traces of one substance may have on another substance (*e.g.*, impurities in metals). The highest hydrate of sulphuric acid contains only 0·1 per cent H_2SO_4, yet the breaks at the extreme ends of the curve are comparatively more marked and more certain than most of the others. The author has recently given a striking proof of the existence of the break in the heat curve of sulphuric acid at 0·3 to 0·4 per cent, in the fact that the heat of neutralisation of this acid becomes "normal" when this break is recognised.

The progress of differentiation was always applied to the experimental numbers themselves in the first case, but for the second differentiation it was necessary, owing to the magnitude of the experimental error, to take the smoothed first differential curves, and not the experimental numbers. With the heat results, where the error is comparatively large, the first differentiation was performed on the curve representing the results as well as on the experimental numbers.

The author mentions a striking proof that the character of the second differential is not attributable to any peculiarity in the manner in which he drew the first differential figure from which it is deduced. When the contraction produced on mixing sulphuric acid and water in different proportions is plotted out, a figure results utterly unlike that representing the densities, and the first differential figure (obtained from the experimental numbers) which it gives is also quite unlike the first differential from the densities, yet these two dissimilar figures give, on a second differentiation, figures which are identical with each other, both as to the inclination of the straight lines of which they are composed, and as to the points at which these straight lines meet.

It may be noted that the maximum contraction on mixing sulphuric acid and water does not occur at a point corresponding to $H_2SO_4,2H_2O$, as has hitherto been supposed, but at a point some 4 per cent below it, a point coincident with any break.

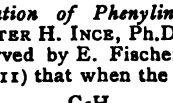
The final conclusion which the author deduces from his work is the absolute rejection of any theory of dissolution other than the hydrate theory.

49. "*The Expansion of Water and other Liquids.*" By S. U. Pickering.

The author gives some determinations of the density of water at different temperatures which indicate sudden changes in the rate of expansion at about 10° and 18°. On examining the results obtained by Pierre, Kopp, Rosetti, Matthiessen, Solly, Despretz, and Hagen, he obtained further evidence of these changes, as well as of another change at 50—60°. Pierre's results also show marked changes at 0° and 2·5°. Pierre's results with eleven organic acids were then examined, and in most of them there appeared to be sudden changes at certain temperatures, which temperatures were different for different liquids. Nearly all of these results show that the densities of liquids, when plotted against temperature, form a series of parabolic curves of the second order, not meeting tangentially, and differentiating, therefore, into a series of straight lines which do not meet at the points where the breaks occur.

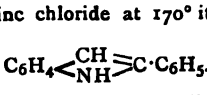
50. "*The Formation of Phenylindoles by Isomeric Change.*" By Walter H. Ince, Ph.D.

It has been observed by E. Fischer and Th. Schmitt (*Ber.*, 1887, 1071, 1811) that when the phenylindole—

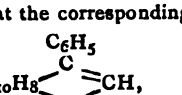


is heated with zinc chloride at 170° it is converted into the isomeride—

The author finds that the corresponding naphthindole,—



and the methylphenylindole,—



undergo change in a similar manner, although action takes place neither so easily nor so completely as in the simpler case.

51. "*An Improved Soxhlet Extractor and Vacuum Distilling Apparatus.*" By J. Lewkowitsch, Ph.D.

The author attaches a tap at the bottom of the syphon-tube of the Soxhlet extractor, by means of which a few drops of the solvent as it runs from the extracted substance can be withdrawn to ascertain whether the extraction is complete.

For use in distilling small quantities of liquid which froth, and through which it is necessary to pass an air-current while distilling under reduced pressure, he describes a flask made by inserting and sealing in, just above the bulb of a Wurtz flask, a tube which passes down nearly to the bottom of the flask, and there terminates in a fine point.

He also describes a simple adapter for use in fractional distillation under reduced pressure.

At the next meeting, on June 6th, the following papers will be read:—

"Experimental Researches on the Periodic Law." By Dr. B. Brauner.

"The Amylodextrin of W. Naegali." By H. T. Brown and G. H. Morris, Ph.D.

"The Determination of the Molecular Weights of the Carbohydrates." Part 2. By the same.

"Researches on Silicon Compounds." Part 5. By Prof. Emerson Reynolds, F.R.S.

"The Isomerism of the Alkyl Derivatives of Mixed Diazoamido-Compounds." By Prof. Meldola, F.R.S., and F. W. Streatfeild.

"The Atomic Weight of Zinc." By Dr. Gladstone, F.R.S., and W. Hibbert.

"The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water." By R. Warington, F.R.S.

"The Product of the Action of Sulphur on Resin." By G. H. Morris, Ph.D.

PHYSICAL SOCIETY.

May 11, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. A. Clegg, Prof. V. B. Lewis, and Mr. W. Robinson were elected Members of the Society.

The following communications were read :—

"*On an Electrostatic Field produced by Varying Magnetic Induction.*" By Dr. O. Lodge, F.R.S.

This paper describes a research made with the object of finding some connection between static electricity and magnetism. Several methods of attacking the problem, such as rotating or varying the strength of magnets in the neighbourhood of delicately suspended charged bodies, are indicated, and the one selected was based on an idea of Mr. A. P. Chattock, who conceived that a charged body in the vicinity of a closed magnetic circuit would be affected by varying the magnetic induction. From the theory of the effect it is shown that the magnitude of the quantity sought is exceedingly small, for the expression involves the inverse square of the velocity of light. The E.M.F. induced in any closed curve round the magnetic circuit or solenoid by varying the induction, I, is given by $e=\frac{dI}{dt}$ (1). If an E.M.F, e, act on a charge, Q, at a distance r from the axis of the solenoid, the work done in one revolution will be e Q and e Q = F.$2\pi r$ (2), where F is the mechanical force. Now, if the E.M.F. in (1) is the same as that in (2) the impulse given to the charged body by destroying the induction will be—

$$\phi=\int_0^\infty F\,dt=\frac{IQ}{2\pi r}\text{ (3).}$$

Since $I=\frac{4\pi n C A \mu}{l}=\mu C$ times a length, and $Q=s V=KV$ times a length, $\therefore \phi=\frac{K\mu C V A}{2\pi r}$ (length)^3 and $K\mu=\frac{1}{\text{“}v\text{”}^2}$

$\therefore \phi \propto \frac{1}{\text{“}v\text{”}^2}$.

The magnetic circuit actually used was a wire gramme ring of trapezoidal section wound with copper over a part of its periphery. The indicating apparatus was a suspended needle consisting of two oppositely charged bodies carried on a small shellac arm to which a mirror or pointer was attached, and was suspended vertically in the plane of the ring. A microscope was used when the needle had a pointer attached. Great difficulty was experienced from Foucault currents when metallic films were used for the needle, and the magnetic properties of other semi-conductors tried further complicated the matter. Eventually the charged bodies were made of paper in the form of cylinders ¼ inch diameter and ⅝ long.

Considerable trouble was caused by the electrostatic action between the needle and exciting coils, and various methods of screening were tried and abandoned, and subsequently the wire was replaced by a single spiral of copper ribbon, the outer turn of which was put to earth. Observation was rendered difficult owing to the wandering of the zero when the needle was charged, but this was minimised by suitably shaping the contour of the needles surroundings. Heat also created considerable disturbance, and the connection currents were cut off by a series of concentric cylinders of tin plate.

The method of observation was to charge the two insulated parts of the needle and then reverse the magnetising current in synchronism with the period of the needle, noting whether the amplitude of any residual swing could be increased or diminished according as the impulse assisted or opposed the motion. In this way slight indications have been observed, and the effects reverse when the charges of the cylinders are reversed.

In explaining the theory of the experiment the author made use of a simple transformer consisting of an ordinary hank of iron wire wound over with insulated copper and provided with several secondary coils, and by it he demonstrated that the primary current increases on closing the secondary, due, as was shown, to the decrease of self induction of the primary caused thereby.

Prof. Fitzgerald, in answer to a question from Dr. Lodge as to the influence of screens, said he had not fully considered the matter in this particular case, and as the general effect of screens depended on the square of "v," the subject required careful treatment. As a means of checking the results obtained by Dr. Lodge he suggested calculating the impulse and seeing whether its magnitude approximately corresponds with that observed. Commenting on an idea for carrying out a similar experiment attributed to him in the paper, in which a charged gold leaf is placed between the poles of a magnet, Prof. Fitzgerald said he had been misunderstood, for he had conceived a disc parallel to the faces of the magnets, which, when excited, should cause the disc to turn in its own plane.

Referring to the equations for mechanical force given in "Maxwell," § 619, he pointed out that the coefficient of e in the equation $X=cv-bw-e\frac{d\Psi}{dx}-m\frac{d\Omega}{dx}$ ought to be P, where $P=c\dot{y}-b\dot{z}-\frac{dF}{dt}-\frac{d\Psi}{dx}$, and considered it very important that the existence of the term $e\frac{dF}{dt}$ should be tested experimentally.

Prof. S. P. Thompson mentioned some experiments on which he was engaged by which he hoped to show electric displacement in continuous dielectric circuits, such as a link of gutta-percha. Up to the present the experiments had not been successful, owing to his inability to place the two gramme ring coils used into such relative positions as to give silence in the telephone connected with the coil used as secondary when currents were sent through the primary.

Prof. Ayrton suggested that Dr. Thompson's difficulty may arise from the fact that such rings do produce considerable external field, even when carefully wound.

Prof. Fitzgerald requested Dr. Thompson to investigate the effects of displacement currents, and of changing vector potential, and pointed out that in a single medium the former can produce no magnetic effect. As regards fields containing different media, he said the calculations would be complicated by the spurious charges on the separating surfaces.

Dr. Lodge, in reply, said he had calculated the momentum to be expected in one arrangement of his experiment, in which a suspended aluminium cylinder surrounds one limit of a rectangular magnetic circuit, which formed the core of an induction coil; one end of the secondary was put to the core and the other to the cylinder, thus forming a condenser. The result came out about 10^{-6} dyne second, but he could not say whether such a small quantity was observable.

"*On the Concentration of Electric Radiation by Lenses.*" By Prof. O. J. Lodge, D.Sc., F.R.S., and James L. Howard, D.Sc.

The authors' first attempts at concentration were made with mirrors on a comparatively small scale, and owing to the difficulties experienced it was considered advisable to try lenses. Two large cylindrical ones of plano-hyperbolic section were cast of mineral pitch in zinc moulds, the plane faces being nearly a metre square, the thickness at vertex 21 c.m., and each lens weighed about 3 cwt. The eccentricity of the hyperbola was made 1·7, to approximate to the index of refraction of the substance. The lenses were mounted about six feet apart, with their plane faces parallel and towards each other on a table in the college corridor, and an oscillator was placed about the principal facial line of one of them at a distance of 51 c.m. from the vertex. The field was explored by a linear receiver made out of two pieces of copper wire mounted in line on a piece of wood, and the air-gap between their inner ends was adjusted by a screw. When the oscillator worked satisfactorily the receiver would respond at about 120 c.m., and with the lenses the distance was 450. The receiver responded anywhere between the lenses and within the wedge between the

second lens and its focal line, the boundaries being clearly defined, but no special concentration was noticed about the focus. Interference experiments were carried out by placing a sheet of metal against the flat face of the second lens, and determining the positions of minimum intensity between the lenses. The distance between these points was 50·5 c.m., corresponding with a wave-length of 101 c.m., whereas the calculated wave-length of the oscillator was 100 c.m.

Prof. Fitzgerald congratulated the authors on their success, and also pointed out that, although large oscillators give good results at distances within a few wave-lengths, yet at greater distances small ones were decidedly superior, owing to the energy of radiation varying as the fourth power of the rapidity. He had recently made experiments on electric radiations analogous to Newton's rings, and had successfully observed the central dark spot and the first dark band. Referring to Dr. Lodge's experiments, he enquired whether any traces of diffraction were observed near the boundary of the bundle of rays between the lenses. Speaking of polarisation experiments Prof. Fitzgerald said waves reflected from films of water exhibited no polarisation, whereas those reflected from non-conductors were completely polarised.

In reply Dr. Lodge said no diffraction effects had been observed, but in the interference experiments to determine wave-length the positions of minimum effect were very decided.

The President, in proposing that the thanks of the meeting be given to the authors of the papers, congratulated the Society on the presence of both Dr. Lodge and Prof. Fitzgerald on the present occasion, when subjects with which they were so well acquainted were brought before the meeting.

OBITUARY.

ROBERT ROMANIS.

The Rangoon College has to record a sad loss, a victim to cholera, in the sudden death on April 13, 1889, of Dr. R. Romanis, D.Sc. (Edin.), F.C.S., F.I.C., &c., the Professor of Physical Science and the Chemical Examiner to Government, Burma.

Dr. Romanis was born in 1853. He joined the Service here in 1878 as Teacher of Science to the then Rangoon High School, now blossomed into a College, and soon it is hoped to ripen into a University. He was appointed Chemical Examiner to Government, Burma, in 1880. In November, 1885, he went up to Upper Burma with the expeditionary force in the last war as a scientific officer attached to the force.

His sudden death must be a startling shock to all, and most of all to his relations in Scotland; for only yesterday evening, being mail day, I saw a letter of his, addressed to a relative, given to his servant to post. He was working in the laborarory yesterday evening till 5.30 p.m., distilling some Arakan petroleum. He went home two or three times during the day. With his usual quiet manner I noticed, later in the evening, nothing but his low and subdued tone of voice. And next morning—he died at 9 a.m.—his servant, who brings his office box, came and told me that his master had died, at the same time bursting into tears. I went over to his house. The corpse was laid out; his features were still sharp and handsome, though his eyes were somewhat sunken in their sockets. The interment in the Cantonment Cemetery took place this evening. As the college is closed, the boys having gone home for the holidays, the funeral procession missed the attendance of the boys in their bright-coloured national costume. Still the funeral did not lack attendance. The Chief Commissioner himself, besides other officials and non-officials, graced the ceremony. It was a fair gathering. As Dr. Romanis was a captain in the Rangoon Volunteer Rifles he had a military funeral, and three volleys were fired into the air after his coffin was lowered.

Three days ago he brought some weeds, dug from some muddy ponds near the Shway Dagon Pagoda. He was looking for diatoms; and he caught, according to some, the cholera germs from those mud pools. If so, he died a martyr to science! Four or five years ago he sent home to Mr. W. Joshua, of Cirencester, some of these low organisms from, I think, these very pools, and Mr. Joshua was fortunate enough to discover about a dozen new species of Desmids.

Though it does not beseem me to speak of myself, I must say that to Dr. Romanis I personally owe a debt of gratitude. He first led me to drink at the fountain of science. To his guidance and care I owe my study of chemistry. He selected me to be his assistant, five years ago, from among his students. I, on my part, did my duty to him ungrudgingly and in love. I can scarce believe that the once familiar face will pace the laboratory no more; that those footsteps will be heard no longer where they had been heard for years! So our college sees extinguished its brightest star in its firmament in a professor gentle, kind, conscientious, and generous—at once loved and respected. His death carries sorrow to many hearts, and he died young—so die those who the gods love.

The last two years he was engaged in examining the products of the distillation of teak. He communicated some of his results to the Chemical Society, but the examination is still unfinished. Besides the records of his annual reports, some of his separately published papers may be noted:—"Coal Outcrops in the Henzada District"; "Oil Wells at Yenangyoung"; "Ash of Wood and other Forest Products"; "Notes on Usar and Reh Soils"; "Experiments in the Cultivation of Sugar-cane in 1882—83." Three weeks ago he applied for three months' privilege leave to go home.

John Tsawoo White.

NOTICES OF BOOKS.

The Patents, Designs, and Trade Marks Acts, 1883—1888 Consolidated, with an Index. By Lewis Edmunds, D.Sc., LL.B., Barrister-at-Law. London: Stevens and Sons, Limited.

The compilation before us will prove of great value to patentees, actual or intending, as well as to patent agents. Not the least of its merits is that it exhibits the manifold defects of existing British patent law in all their deformity. The functions of the examiners here appear very much to resemble those of King Log, whilst those of the patent-examiners in Germany and the United States much more closely resemble those of his successor, King Stork. We have known a German examiner, after having been fairly beaten out of the objections which he had raised to an application for a patent, to bring forward a new one, not mentioned at all in his first report, and to hold to it. We have also known a case where an American examiner could not be got to see the difference between a hydrate and a silicate. One of the most useful duties which, by the Act of 1883, devolved upon the examiners, has been done away with by a later enactment. It was to the effect that if the invention comprised in two applications for patents is found to be the same, the comptroller may, on being duly informed of such similarity or identity, refuse to seal a patent on the application of the second applicant. This salutary provision being repealed there is nothing to prevent two, or possibly even more persons, from obtaining patents for the same invention, and becoming consequently involved in litigation.

The cardinal flaw in our patent system is that an alien not domiciled in the United Kingdom may not only obtain, but continue to uphold, a patent without ever working or allowing it to be worked on British ground. As it is done in other countries, we ought to hold such patent at once invalid and cancelled, unless worked on a commercial scale within a term of, say, three years. This brings us to the point that our patent reciprocity with foreign states is very one-sided. We grant much more to foreigners than they grant to us in return. An alien may obtain a British patent without any scrutiny as to the novelty or the practicability of the process, and may, provided he pays the fees, uphold it for the full term of fourteen years, though he may never work it at all on British soil. On the contrary, a British subject can obtain patents in foreign countries only after an examination more stringent than what a native of such country would have to meet, and when he has actually received a patent he can uphold it only by continuous *bonâ fide* working in the country in question.

One very important industrial country has in its patent system a proviso that if a foreigner applies for a patent and some native thinks proper to come forward and declare upon oath that he has invented the same process, but has been prevented from patenting it by lack of means, by other occupations, absence from home, or sickness, he is pronounced to be the first and true inventor, and the foreigner finds his application dismissed.

We might with advantage borrow and extend one of the features of the German patent law, which refuses protection to proprietary medicines. Did we not only do this, but refuse trade-marks to such concoctions, to alleged medical appliances other than medicines, to "foods" and substitutes for foods, a death blow would be struck at quackery, and many phases of adulteration would cease to exist.

Another shortcoming of our patent system is its limited extent in space, covering merely the United Kingdom and the Isle of Man. Under what is known as the "old law" a patent for a slight additional fee could be obtained covering the whole of "Her Majesty's dominions and plantations abroad." On passing what up to 1883 was called the "new law" this vital clause was quietly struck out. We need an Imperial patent-law, which would give an immense stimulus to invention and industry. A mere stroke of the pen would do this for India and the so-called "Crown colonies." Those colonies which have quasi-independent legislatures could easily be prevailed upon to accept an agreement which would give them, no less than the dwellers in the Home Kingdoms, increased privileges.

Examination of Water for Sanitary and Technical Purposes. By H. LEFFMANN, M.D., Ph.D., and W. BEAM, M.A. Philadelphia: P. Blakiston, Son, and Co.

IN their preface the authors remark that "there are several special manuals at hand, but they are limited in scope and contain much matter which does not bear on the problems that confront the sanitary and industrial chemist, devoting much space to the description of processes that are not generally employed, and to the presentation of the details of a local professional quarrel." It would be idle on our part to affect misunderstanding of the last dozen words. But we know of only one special manual in which the details of the "quarrel" in question —which was something very much more than local— have been lately reproduced.

As to the scope of the manual before us, it gives no special directions for the analysis of urines, sewage, sewage-effluents, or industrial waste waters. There are remarks on the detection of a fungus "supposed to be peculiar to sewage." But as the occurrence of this fungus is afterwards pronounced due to the presence of phosphates it cannot be the notorious *Beggiatoa alba*, which grows not merely in sewage but in the waste waters from Leblanc alkali works and from natural sulphuretted springs.

Among the technical applications of water one only—its use for generating steam—receives any special notice.

On the "professional quarrel" above mentioned the author tacitly pronounces his verdict by omitting all mention of the Frankland and Armstrong process for the determination of organic nitrogen.

The well-known Clark process for the determination of the hardness of waters is explicitly rejected in favour of a process devised by Mr. Hehner. A colorimetric process for the determination of nitrates and nitrites is given in preference to the methods hitherto in use.

For the estimation of ammonia, free and "albumenoid," we find here the Wanklyn and Chapman process with unimportant modifications in the apparatus required. For ascertaining the "oxygen-consuming power" the authors describe Dr. Tidy's method, and mention the processes of H. Fleck and A. R. Leeds. They remark, however, that the two latter processes are open to the same objections as is the use of permanganate, and do not seem to possess any decided advantage.

For the determination of free oxygen the authors make no mention of Gerardin's "hydrosulphite" process, but give the method of Mohr as modified by Blarez and a pyrogallol process. It may somewhat surprise the reader to find a method for the detection and estimation of boric acid—a compound, we should think, of exceedingly rare occurrence in drinking-waters, from whatever source. We are glad to see that among the poisonous metals possibly present chromium is not overlooked.

The determination of the specific gravity of waters is pronounced to be, in the majority of cases, not essential. Mr. Wanklyn is of a different opinion, and a medical contemporary, in reviewing the seventh edition of his "Water Analysis," regards the new chapter on this point as embodying "a distinct practical advance."

A method is given for the determination of phosphates, but the authors, in accordance with Mr. Wanklyn, consider that all beyond very minute proportions will be precipitated, though they agree with Mr. Hehner that their presence in noteworthy quantities should be regarded with suspicion. The hardness of a water they consider of little sanitary importance.

Into the question of living organisms in water and their possible effects the authors enter but slightly, rightly judging that bacteriological examination is as yet of uncertain value as regards the potability of water. Upon the purification of water-supplies they express very sound views. They admit, with Dr. Frankland, that carbon filters sometimes seem to act as a hot-bed for the development of microbia. Stone and sand filters they regard as worthless, that is, for the elimination of living organisms. Spongy iron was found to reduce the microbia by about one-half in the best cases, but the unglazed porcelain filters on Pasteur's principle, and also the asbestos filters, give a filtrate practically free from micro-organisms. They quote from Dr. P. Frankland important results as to the removal of organised matter from water both by occlusion (*i.e.*, agitation with finely-divided absorbent solids) and by precipitation. From their own observations they state that a precipitate of aluminium or of ferric hydroxide carries down with it all suspended matters as a large proportion of the dissolved organic matters.

A Table of Specific Gravity for Solids and Liquids. (*Constants of Nature*, Part I.). New Edition, Revised and Enlarged. By FRANK WIGGLESWORTH CLARKE, Chief Chemist, U.S. Geological Survey. Published by the Smithsonian Institution. London and New York: Macmillan and Co.

THE author's "modest work," as he calls it, is a precious and enduring monument of protracted labour and of self-abrogation in the cause of Science. The tables in the

present edition have been greatly extended, and now include the specific gravities of 5227 distinct substances and 14,465 separate determinations. In the original edition there were given only 2263 substances. The boiling- and melting-points have been omitted, except where they seemed necessary for the identification of a compound, as that requirement is fully supplied by the tables of Prof. Carnelley.

The Metallurgy of Gold: A Practical Treatise on the Metallurgical Treatment of Gold-bearing Ores, including the Processes of Concentration and Chlorinisation and the Assaying, Melting, and Refining of Gold. By M. Eissler, late Assistant Assayer of the U.S. Mint, San Francisco. Second Edition, enlarged. London: Crosby Lockwood and Son.

In November last we had the pleasure of examining the first edition of this manual, and we felt bound to pronounce it valuable to all persons interested in the metallurgy of the precious element. But the fact of a second edition having been required after the lapse of a few months is a more decisive recommendation than any in our power to offer.

The book in its present form is not a mere reprint, but has been enlarged by about 150 pages. The added matter includes an account of the more recent developments of the chlorination system, and a chapter on smelting gold ores and refining gold bullion.

In view of the not improbable circumstance of a third edition being shortly required, we should suggest that an account of the geological features of the gold-bearing districts of Australia and South Africa might be usefully added.

Stellar Evolution and its Relations to Geological Time. By James Croll, LL.D., F.R.S. Author of "Climate and Time," "Climate and Cosmogony," "Philosophy of Theism," &c. London: Edward Stanford.

The age of the sun is a most important question, since, if established, it yields an outside limit in time for the past duration of our earth, and of course for the evolution of its geological features and its organic inhabitants, probably also of the elements of which it is composed. No little sensation was therefore created some time ago when a most eminent physico-mathematician announced, as the result of his calculations, that the sun could not have been supplying light and heat to the earth for more than twelve million years. Of this term, not much more than the half could be allowed for the age of life upon the earth.

This statement was hailed in certain quarters as fatal to the results of geology no less than to the Lamarck-Darwinian doctrine of organic evolution. The rejoicers, however, had not taken the trouble to ascertain what Sir W. Thomson had really demonstrated. He had shown that the sun cannot have been irradiating our globe for more than twelve million years *if* gravitation be the sole or the main source from which his heat has been derived. But this is not proven. Mr. Croll shows that another theory of the origin of solar heat is possible. Instead of the sun having been constituted by particles of matter, large or small, drawn together by gravitation, he proposes the "impact theory," that our sun was formed from a hot gaseous nebula, produced by the colliding of dark stellar masses. He argues that eternal motion is just as legitimate an assumption as eternal matter. "If the masses were created they may as likely have been created in motion as in rest; and if they were eternal—a view which he subsequently combats—they may as likely have been eternally in motion as eternally at rest." If the sun has thus been formed his original quantum of heat may easily have been so great that the past 100,000,000 years, or even a far longer time, would not suffice for its exhaustion.

Mr. Croll contends that on his theory the absolute motion of stars is due, not to the influence of gravity, but to motions which originally belonged to the two component masses out of which the star arose. "We know that there are stars, *e.g.*, 1830, Groombridge, which have a far greater velocity than can result from gravitation."

The author next marshalls, in support of his impact theory, evidence as to the heat of the sun drawn from geological and biological considerations. This evidence, to persons capable of appreciating the facts, is perfectly overwhelming. We have all along held, with Mr. Croll, that "the grounds upon which the geologists and the biologists found the conclusion that it is more than twenty or thirty millions of years since life began on the earth are far more certain and reliable than the grounds upon which the physicist concludes that the period must be less." He adds, very justly, "the only real ground that the physicist has is that according to the theory which he holds of the origin of the sun's heat a longer period is not possible." The reply of the geologist and the biologist is, "then your theory must go, since it leads to a result not reconcilable with facts."

In the third part the author adduces evidence in support of the theory from the pre-nebular condition of the universe. He sums up the views of Prof. Winchell, of Mr. C. Morris, of Sir W. Grove, of Prof. Clarke, Mr. Norman Lockyer, Dr. T. Sterry Hunt, Graham, Sainte Claire Deville, M. Berthelot, Brodie, Prof. Oliver Lodge, and especially of Mr. Crookes, whose address before the Chemical Section of the British Association in 1886 is largely drawn upon. Dr. G. Johnstone Stoney's inquiries into the pre-nebular condition of matter are also taken into account.

All men of science who pay due heed to the ultimate principles to which they are perforce brought in the course of their researches will find this work deserving a much more thorough scrutiny than space has here allowed us to give it. Mr. Croll has, at all events, swept away a cloud with seemed at one time likely to obscure the general significance of Evolution.

Variations in the Composition of Milk.— Harald Faber (*Tidskrift for Landökonomi*).—From the results of about 50,000 analyses made in the laboratory of the Dairy Supply Company the author concludes that the dry matter less fat is an almost constant value (8·7 to 8·8). The fluctuations in total solids depend almost entirely on variations of the fat. The evening milk contains more fat and more total solids than the morning milk. In October and November the milk is richer in fat and total solids than in other parts of the year.

The Formation of Nitre Earths.—A. Muntz and V. Marcano.—The attention of the authors has been drawn to caves not inhabited by winged animals, and having no superficial deposits of guano, yet containing soil richly charged with nitrates, On boring there have been found the presence of the bones of large mammals abundantly and uniformly distributed through the whole mass of nitre-earth. These bones crumble to powder if touched, and are composed almost exclusively of calcium phosphate; calcium carbonate is totally absent, and there are mere traces of organic matter. The nitre produced at the expense of the nitrogenous organic matter, and secured from the action of rain, has been able to accumulate. The calcium carbonate of the bones has served in nitrification and reappears as calcium nitrate. The brittleness of the bones is due to the action of the nitric ferment. Such caverns abound in Venezuela, not only in the littoral mountains but in the flancs of the Cordillera. The beds reach and even exceed ten metres in thickness, the soil containing calcium nitrate from 4 to 30 per cent and calcium phosphate 5 to 60 per cent.—*Comptes Rendus*, Vol. cviii., No. 17.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 17, April 29, 1889.

On Obtaining Photographs in Accurate Values by the Use of Coloured Glasses.—G. Lippmann.—The author mentions the well-known defect in photographs; that, except blues and whites, objects are imperfectly represented, since the plate is much more sensitive for blue rays than for any others, so that an exposure which is sufficient for the blues is quite insufficient for other colours. To obviate this inequality he places a blue glass in front of the lens and exposes long enough for the blue rays to act upon the plate. He then substitutes a green glass for the blue and exposes again, taking care not to touch the camera or displace the object. Finally he uses a red glass. The result of this triple exposure is to give clear photographs, in which green foliage, yellow or red draperies, &c., instead of giving brown tones, are rendered as in a good engraving.

Losses and Gains of Nitrogen in the Experimental Field of Grignon from 1875 to 1889.—P. P. Dehérain.—The results of the observations made at Grignon may be summed up as follows:—All the plots containing notable quantities of combined nitrogen (2 grms. per kilo) and cultivated without manure have lost considerable proportions of nitrogen. These losses greatly exceed the demands of the harvests. They are by no means equal for all crops, being very rapid in soils which have been planted with beets, rather slower for feeding maize, and still slower for soils which have yielded potatoes and wheat. When, after several years of cultivation without manure, the soil has been impoverished down to 1·45 to 1·50 grms. of nitrogen per kilo. the losses ceased and a gain in nitrogen set in. This gain, trifling in soils under varied cultivation, has been considerable for grass-lands.

On the Alloy of the Standard Kilogramme.—J. Violle.—The material adopted is platinum alloyed with 10 per cent of iridium. The alloy has been prepared with the greatest care by Mr. Matthey (Johnson and Matthey), who has succeeded in surpassing decidedly the degree of chemical perfection required by the International Commission, as proved by the analyses of MM. Stas and Debray. The alloy in question behaves like a mixture, both as regards its specific gravity and its specific heat. For this alloy, and probably for every other metal which is physically homogeneous, the sp. gr. is a perfectly defined number, which, when once reached, cannot be modified neither by pressure, nor by tempering, nor by the most violent blows.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 4.

Determination of Nitrogen in Arable Soils.—M. Berthelot and G. André.—From the *Comptes Rendus.*

The Loss of Gaseous Nitrogen during the Decomposition of Organic Substances.—Th. Schlœsing.—Also noticed under *Comptes Rendus.*

An Exact Experiment in Manuring Barley.—Dr. J. Hanamann (*Oester-Ungar Zeitschrift Landwirthschaft*).—Ammonia with superphosphate or nitre and superphosphate must be applied for a maximum production.

Manurial Experiments on Oats and Summer-Wheat with Nitre and Superphosphate.— M. Roth (*Sächs. Landwirth. Zeitschrift*).—The use of small quantities of phosphoric acid does not affect the yield of wheat, and in larger doses it occasions a decrease. In case of oats it reduces the financial result in whatever quantity.

Results of Comparative Manurial Experiments with Basic Slag and Superphosphate.—Dr. E. Meissl.—For autumn dressings and where it is desired to give a supply of phosphoric acid for several years, basic slag can mostly be substituted with advantage for superphosphate. For spring dressings and in all cases where phosphoric acid has to be supplied for immediate assimilation slag is never equal to superphosphate.

Increase of Crops by the Use of Ferrous Sulphate in the Years 1887-88.—P. Margueritte-Delacharlonny.—Copperas, if applied to vines, is said to increase the yield and to protect the vineyards aggainst the *Phylloxera* and chlorosis. An application of 800 kilos. copperas per hectare was found to restore meadows attacked by cuscuta. The yield of clover and lucerne was increased, by the application of the same agent in smaller proportions, from 25 to 33 per cent. A satisfactory result was also obtained with potatoes and grain.

The Suppression of the Potato-disease by Means of Iron Sulphate.—P. Margueritte-Delacharlonny.—The results obtained have been very favourable. The sulphate is best applied when the young plants have reached the height of a few centimetres.

An Error in the Determination of Nitrates in Soils.—Michele Giunti.—On extracting nitrates from soils by means of water the results were the lower the longer the water was allowed to act. These losses were entirely avoided if the samples were sterilised by means of chloroform.

Journal de Pharmacie et de Chimie. Vol. xix., No. 8, April 15, 1889.

Researches on the Saccharine Matter of Some Species of Fungi.—Em. Bourquelot.—The sugars detected have been trehalose and mannite. The former is found in mushrooms when in a state of vigorous vegetation, but disappears if they are slowly dried at a low temperature.

On Gold Arseniate.—P. Carles.—A substance lately introduced into medical practice under this name is merely a crude mixture of gold chloride and sodium arseniate.

The Identity of Analgesine and Antipyrine.—A. Petit.—The author demonstrates the identity of these preparations.

On the Dangers which may Arise from Tin Covers containing Lead.—E. Leger.—The covers in question are attached by means of a hinge to stoneware jugs used for containing alimentary or medicinal matter. In such a lid M. Léger finds 76·83 per cent of lead and only 22·41 of tin. Such an alloy is, of course, readily attacked by the organic acids.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lectures). "Heat Engines other than Steam," by H. Graham Harris.
Tuesday, 28th.—Institute of Civil Engineers, 8. (Anniversary).
—— Royal Medical and Chirurgical, 8.30.
—— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.
—— Society of Arts, 8. "The Westinghouse Alternating System of Central Station Electric Lighting in the United States of America," by James S. Humbird.
Wednesday, 29th.—Society of Arts, 8. "The Science of Ventilation as Applied to the Interior of Buildings," by D. G. Hoey.
Thursday, 30th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
Friday, 31st.—Royal Institution, 9. "An Attempt to Apply to Chemistry one of Newton's Principles," by Professor Mendeleeff.
—— Society of Arts, 8. "Indian Wheats," by John McDougall.
Saturday June 1st.—Royal Institution, 3. "The Classification o the Sciences, Historical and Critical," by Prof. W. Knight.

THE CHEMICAL NEWS.

Vol. LIX. No. 1540.

ON THE

PRESENCE OF TIN IN CERTAIN KINDS OF SUGAR, A MEANS OF DETECTING IT, AND THE PROBABLE INFLUENCE OF THIS SUBSTANCE ON THE PUBLIC HEALTH.

By Dr. T. L. PHIPSON, F.C.S. (London),
Formerly of the University of Brussels, and late Assistant Professor in the Laboratoire de Chimie Pratique, Paris;
Member of the Society of Chemical Industry, &c.

A large sample of sugar purchased in London at a well-known Stores as "Demerara" was recently submitted to me for examination. It had a golden yellow colour, was rather moist, and, on dissolving in water, left a considerable amount of residue and formed a solution that was cloudy.

Lady E——, who desired this sugar to be analysed, informed me that her servants objected to use it, but without giving any reason; she herself liked it on account of its intense sweetness, and had used it for about six weeks, but at the end of that time she had suffered from diarrhœa, *accompanied by pain*, which she had not experienced before in similar attacks, and she fancied the sugar may therefore have been the cause of this attack. She left off using this kind of sugar and the ailment ceased in the course of a few days.

Such was the information given to me with the sample in question. The solution of this sugar had a golden colour, a very agreeable aromatic flavour, and a very sweet taste. I made three analyses of the sugar and found that it contained 0·04 per cent of oxide of tin, a considerable amount of glucose, and a large amount of ash (2·70 per cent) rich in lime, with some oxide of iron and phosphate of lime. Tin is the principal impurity to which it is necessary to draw attention.

In June, 1881, I was requested to attend a meeting of the West India Committee in London, after having detected a minute quantity of oxide of tin in some samples of sugar sent to me for analysis by some members of the committee. On that occasion I was informed that chloride of tin was used in preparing certain kinds of sugar for the market, in order to give them a golden hue which was much admired; and my opinion was asked as to the influence which the small amount of tin found in the samples analysed might have upon the health of the consumers. I had only two samples to examine, and the quantity of tin in them was so small that I stated my belief that it would exert no noxious influence if it did not go beyond that figure (0·001 per cent), but that great caution would have to be observed. It appears, however, that since then the quantity has increased considerably, and the time has perhaps come when this process of "curing" sugar will have to be very closely looked into.

There are several means by which tin can be detected in sugar and its amount accurately estimated, but certain precautions must be carefully observed, otherwise erroneous results will ensue. The method I follow is this:—Not less than two ounces of the sample are taken, dissolved in a certain quantity of cold water, and, *without separating the residue*, the solution is rendered slightly acid by hydrochloric acid; it is then saturated with sulphuretted hydrogen. For the two ounces of sugar I take about a pint of water and one to two drachms of hydrochloric acid. When the solution is saturated with sulphuretted hydrogen, the bottle is covered with a plate of glass, and the solution *allowed to deposit for at least forty-eight hours*. The clear liquid can be mostly decanted off and the deposit collected upon a filter and washed. It contains the sulphide of tin along with the insoluble impurities. The former is separated by washing with sulphide of ammonium, from which solution the pure sulphide of tin is precipitated by hydrochloric acid, added *just in sufficient quantity only*, and the liquid again allowed to deposit for forty-eight hours. By this means *the whole* of the sulphide of tin is collected. It is dried, and transformed by calcination, with the usual precautions, into stannic oxide, which is weighed.

With regard to the action of tin compounds upon the animal economy, we must remember that by its chemical reactions oxide of tin resembles the oxides of antimony and arsenic very closely, both of which are powerful poisons. Nevertheless Orfila compares the action of tin salts upon the tissues more to that of bichloride of mercury or corrosive sublimate. As tin salts are not used in therapeutics we have little experience of their effects in very small doses; but chloride of tin (stannous chloride) has been long known to be a very dangerous substance. Dr. Christison, in his work on "Poisons," relates a case of voluntary poisoning by it, and Meinel (1851) refers to another case in which chloride of tin had been formed by the action of impure damp salt upon some metallic plates. The poisoning which has occurred of late years by the use of tin vessels has been attributed to lead, the tin being largely adulterated with the cheaper metal.

Wm. Stone, in his "Toxicological Tables" (translated into French from the 11th English Edition by Acar, Pharmacist to the Military Hospital at Antwerp, 1853), says, under the head of "Tin, chloride, hydrochlorate, or oxide," that in poisonous doses these substances produced the following symptoms:—"Nauseous styptic taste, constriction of the throat, vomiting, and *pain all over the abdomen*, abundant stools, pulse small, hard, and frequent, convulsive movement of the face and limbs, sometimes paralysis; death generally occurs when the chloride or hydrochlorate has been taken."

Other remarks on the toxic action of tin salts are to be found in the *Annales d'Hygiene Publique*, by Poumet (1845) and Gobley (1869). In more recent times we have the experiments of Ungar and Bodländer (1887), with several compounds of tin, and, among others, stannous chloride and tartrate of tin and sodium. These experiments were made on frogs, rabbits, and dogs, and in all cases toxic symptoms ending in death ensued with large doses, whilst with very small doses repeated for some time the "results were like those of other metals which gradually undermine the health."

Such being the case, and in view of the enormous consumption of sugar by all classes of people, I am of opinion that the use of tin salt, or any other noxious ingredient, in curing or beautifying sugar, is a practice which should not be tolerated. Taking the above analysis as a fair average result (for the sample weighed about five pounds) it shows that any person who, like myself, consumes about four ounces of sugar per diem, would assimilate nearly 7-10ths of a grain of tin oxide (but probably in the shape of some organic compound or as chloride) every day, if he used this particular kind of sugar. Or, say, that anyone took only a quarter of that amount, one ounce a day, he would absorb nearly 2-10ths of a grain of tin oxide per diem, or close upon 1½ grains a week; and, as metallic poisons have a tendency to accumulate in the liver or other organs, there is no saying how much mischief may be induced by a prolonged consumption of sugar containing such an impurity.

Of late years several noxious substances have been proposed and used in sugar-making; the principal of these are *baryta*, *strontia*, and *oxalic acid*. It will, therefore, become the duty of all chemists who devote themselves to the public health analyses, that is, to the detection of impurities or adulteration in foods and drugs, to search carefully for the substances mentioned, and make the results widely known. A sugar which shows, on analysis, as much as 98 or 99 per cent of cane-sugar may still con-

tain a sufficient amount of some noxious impurity to prove highly injurious to health.

THE CONTAMINATION OF WATER WITH LEAD.

By THOMAS T. P. BRUCE WARREN.

A RECENT discussion on this subject shows that the contamination of a water supply, when flowing through lead pipes, requires some explanation.

The chemical action of water containing small quantities of CO_2, when passing through an oxidised lead pipe, need only be referred to thus far. The statement that the inner bore of the pipe influenced the amount of lead taken up slightly, deserves more attention. The inner surfaces of pipes vary as the lengths and as the circumferences (D multiplied by 3·1416), so that a pipe double the diameter of another pipe exposes just twice the area to the action of the water. But, supposing that we have the same initial head of water in the two cases, we involve an extra abrading action on the smaller pipe, and consequently, the water-pipes being in other respects alike, we have an increased friction in the smaller pipe, and increased capabilities of being impregnated, which the ratios of D alone will not help us to explain.

The laws affecting friction of water flowing through pipes may be found in any good work on mechanical engineering. When water is exposed to pressure in a lead pipe or tube, so long as the water is quiescent we have no reason to suspect much difference; but when flowing under pressure the conditions are seriously different.

THE ACCURATE DETERMINATION OF CARBONIC ACID AND MOISTURE IN AIR.

By J. S. HALDANE, M.A., M.B.,
and M. S. PEMBREY, Pell Exhibitioner of Christ Church, Oxford.

ON an accurate means of determining carbonic acid and moisture in air depends the solution of a number of problems connected with the respiratory exchange of animals. The present research was undertaken chiefly from this point of view, but is probably of equal interest in connection with questions in meteorology and hygiene.

Both carbonic acid and moisture are present in free air in very minute proportions: the former in the proportion by weight of only about 0·045 per cent; the latter in very varying proportions, under 1 per cent as a rule. It is, therefore, hardly a matter of surprise that the accurate estimation of these substances, and especially of the former, should present considerable difficulty.

The first attempt at a quantitative analysis of the carbonic acid in free air seems to have been made by A. von Humboldt.† His numerous results were, curiously enough, entirely illusory, since he concluded that about 100 vols. per 10,000 of air were usually present. In 1802 Dalton,‡ who made the first approximately correct analyses, reduced the amount to 6·8 vols.; and Dr. Saussure§ had, about 1830, brought it down to a mean of about 4·1 vols. for country air. This result was confirmed by Watson (1834) and Boussingault (1844), who used other methods, and for long was supposed to be nearly correct. Still more recent researches, particularly those of Angus Smith in Scotland,‖ Schulze in Germany, Reiset in France,¶ and Müntz and Aubin in France** and other countries, have gradually reduced it to about 2·9 vols. or less.

There still, however, exists a considerable amount of apparent contradiction on the subject. Even the most recent researches—those made with Pettenkofer's method by Feltz* at Dorpat, and Uffelmann† at Rostock—do not give results agreeing well with those of other observers. Uffelmann's mean result (3·5 vols.) differs by 20 per cent from that obtained previously at the same place by Schultze (2·9 vols.). Feltz's mean result (2·7) is lower than that obtained by previous observers. Not only are the mean results of different observers different, but there is perhaps still greater want of agreement as regards the limits within which the proportion of CO_2 varies.

The methods at present in use for the determination of carbonic acid in air are, practically speaking, of two kinds: (1) those in which the CO_2 is absorbed by standardised baryta-water, which is afterwards re-titrated; (2) those in which it is absorbed by potash, and afterwards liberated by acid and measured in the form of gas.‡

The method best known in this country is that of Pettenkofer,§ or, more correctly, of Dalton‖ and Pettenkofer. In this method a large bottle is pumped full of the air to be examined. A measured quantity of standardised baryta-water is then added, and the bottle closed and shaken, so as to bring the air in contact with the baryta. After a certain time the baryta solution is again titrated, and the CO_2 estimated from the loss of alkalinity of the baryta-water.

Although this method is simple in principle, it is generally admitted that the results obtained by it for free air may easily be very incorrect. The matter will be more fully discussed in the sequel.

For certain cases where the bottle method is not suitable Pettenkofer¶ recommends that a measured quantity of air should be allowed to bubble through a long tube placed nearly horizontally, and containing a known quantity of baryta-water. The CO_2 absorbed by the baryta is estimated in the same way as in the first method. Pettenkofer found that about 5 litres per hour is the maximum rate at which the air can be passed. When large volumes of air are taken for each analysis this method is doubtless much more accurate than the bottle method; but for large volumes inconveniently long periods of time are required. With small volumes of air, such as 10 litres, the error of the method may be, as will be shown later, very considerable.

Reiset** has recently devised an apparatus which allows large quantities of air to be aspirated through baryta-water. With this apparatus he was able to aspirate as much as 100 litres through 300 c.c. of baryta-water in an hour. The absorption of CO_2 appears to have been complete. Each experiment lasted several hours. He used an enormous aspirator, mounted on a cart, and capable of holding 600 litres of water.

The method in which the CO_2 is absorbed by potash, and afterwards liberated by acid and measured in the form of gas, was, in its first form, used by Mangon and

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* Read before the Royal Society, May 2, 1889. (From the Physiological Laboratory, Oxford).

† Gilbert's *Annalen*, vol. iii, 1800, p. 79.

‡ *Manchester Lit. Phil. Soc. Mem.*, 1282.

§ *Annales de Chimie*, vol. xliv., p. 5.

‖ "Air and Rain," p. 59.

¶ *Annales de Chimie*, vol. xxvi., p. 145; vol. xxx., p. 238.

** *Comptes Rendus*, vol. lxxxviii., p. 1007.

* Feltz, "Kohlensäureghalt der Luft zu Dorpat," Inaug.-Diss: 1887.

† *Arch. fur Hygiene*, 1888, p. 262.

‡ A valuable critical account of the methods hitherto used is given by Blochmann, *Liebig's Annalen*, vol. ccxxxvii. (1887), p. 39

§ "Abhandl. der techn. Commission der Bayer. Akad.," vol. ii. (1858), p. 3, and *Liebig's Annalen*, Suppl., vol. ii. (1861), p. 23.

‖ The form finally given to Dalton's method is described in a paper by Watson, communicated by Dalton to the British Association (*Brit. Assoc. Report*, 1834, p. 583). Watson used a large bottle, which he filled with air with the help of a pair of bellows. He then added lime-water, and, after shaking, allowed the bottle to stand for several days, at the end of which time he filtered off the carbonate and titrated with dilute sulphuric acid. Pettenkofer independently invented a similar but improved method. He introduced baryta-water as an absorbent and turmeric as an indicator, and avoided the filtration. Watson's mean result for country air (4·1 vols.) was about the same as that obtained by the earlier observers who used Pettenkofer's method.

¶ *Liebig's Annalen*, Suppl., vol. ii., 1861, p. 23.

** *Loc. cit.*, p. 164.

Tissandier* for balloon experiments. A rough form of this method has been for some years in use at the Paris Observatory. The method has been brought to great perfection by Müntz and Aubin,† whose test experiments show that an accuracy to about 2 per cent of the CO_2 estimated may be attained when 200 litres of air are used. For absorbing the CO_2 they use tubes about a metre long, filled with pumice soaked in caustic potash solution free of CO_2. After the experiment the CO_2 is liberated by the addition of acid, and collected over mercury with the help of a mercury pump. The apparatus necessary for these manipulations is complicated, and considerable skill is required in order to avoid sources of error. With this method Müntz and Aubin confirmed and extended Reiset's conclusions, and found that the mean proportion of CO_2 in country air in the northern hemisphere is about 2·85 vols. per 10,000, and that it very seldom rises above 3·1 or falls below 2·6. The results of these three observers are certainly the most reliable of any hitherto published; and in view of the accuracy of their methods there is little ground for doubting the truth of their general conclusion, in spite of the differences between their results and those obtained by some observers with Pettenkofer's method.

The methods for the determination of moisture present in air are of two kinds. Either the percentage is calculated from the readings of some kind of hygrometer, or it is determined geometrically. The methods of the former kind need not be considered here. The latter method consists in aspirating a known volume of air through an absorption apparatus filled with sulphuric acid and pumice. This method is, in its original form, due to Brunner (see below). It was tested and somewhat altered by Regnault in the course of his well-known research on hygrometric methods. A serious objection is that it only gives accurate average results over relatively long periods (an hour or more), while the percentage of moisture present in air rapidly changes.

Some months ago a number of experiments were undertaken by one of us with a view to devising a new form of apparatus for investigating the respiratory exchange of animals. This apparatus implied a very accurate determination on a large scale of CO_2 and moisture in air. The satisfactoriness of the results of the test experiments with the complete apparatus determined us to investigate more thoroughly the methods of determination used, and to endeavour to make them more widely applicable, not only for physiological purposes, but also in all investigations involving very accurate determinations of carbonic acid moisture in air.

The methods are gravimetric and are not new in general principle. We believe, however, that with attention to the details communicated below these methods will be found to be not only exceedingly convenient, but also very much more accurate than the corresponding methods in ordinary use.

Gravimetric methods of dermining CO_2 in air were at one time much employed, although they have been practically disused since the introduction of Pettenkofer's method. In 1832 Brunner‡ described a gravimetric method. He aspirated the air at a rate of about 30 litres an hour through two absorption tubes. The first contained asbestos soaked in sulphuric acid, and the second, which was three feet long, was filled in the first two-thirds with moist slaked lime, and in the last third with sulphuric acid and asbestos. He tested the completeness of the absorption of the CO_2 by allowing the air to bubble afterwards through baryta solution, which remained clear. The increase in weight of the first tube gave the moisture, that of the second tube the CO_2 in the air aspirated. He says he always obtained for free air results lying between De Saussure's maximum and minimum (3·7 and 6·2 vols. per 10,000).

Brunner's method, with various modifications, has been used by a number of subsequent observers. The most reliable results were those of Boussingault, who obtained with large volumes of air a mean of 4·0 vols. per 10,000 for Paris air.* The results of several other observers were certainly quite unreliable.

In 1856 Hlasiwetz† published a paper in which he criticised adversely the gravimetric method. He made a number of analyses by different forms of this method, and found that not only did analyses simultaneously made often entirely disagree, but that in eleven out of fifty-six analyses the absorption apparatus for CO_2 actually lost in weight. These results he set down partly to unavoidable "errors of weighing," and partly to the fact that CO_2 is absorbed by sulphuric acid. Hlasiwetz's criticisms have been generally accepted as conclusive, and since the publication of his paper the gravimetric method seems to have been almost entirely given up.

Later researches on air have certainly confirmed Hlasiwetz's general conclusions as to the unreliability of the gravimetric method. There is no longer any doubt that the apparent variations found by this method in the amount of CO_2 in air were almost entirely due to imperfection in the method. It will be shown below, however, that these imperfections can be completely removed by attention to details.

Soda-lime has for long been in use as an absorbent for CO_2 in combustions. It was first used by Mulder‡ in 1859, and Fresenius§ has shown its superiority to potash solution, &c. Its use in combustions suggested it as a suitable absorbent for CO_2 in the respiration apparatus already alluded to, and we have made use of it in all our experiments. It has the advantage over lime, baryta, potash, &c., that it can be used in an almost dry condition, so that it loses very little moisture when dry air is passed over it.

For absorbing moisture we have used pumice soaked in sulphuric acid; calcium chloride is quite unsuitable for the purpose, as a single experiment showed us. Our first experiments were made with doubly tubulated absorption flasks of about 100 c.c. capacity.‖ These were arranged so that a current of air was passed through a glass tube at the bottom of the flask, then upwards through the absorbent, and out by a second glass tube opening in the neck of the flask. The flasks were connected in series by means of rubber tubing. The first two were filled with pumice soaked in sulphuric acid; the third with coarsely granulated soda-lime; the fourth with pumice and sulphuric acid; the fifth and sixth, when present, were similar to the third and fourth. When a current of air was passed through the increase in weight of the first flask gave the weight of moisture in the air; the second acted as a test of the completeness of the absorption of moisture by the first; the third absorbed CO_2 from the dry air, but also lost moisture, which was recovered in the fourth. Hence the increase in weight of the third and fourth together gave the CO_2 absorbed from the air. The fifth and sixth together acted as an index of the completeness of the absorption of CO_2 by the third.

Experiment A.

22 litres of air were aspirated through the flasks in fifty-five minutes.

Flask 1.	+0·2114 grm.	
,, 2.	+0·0010	
,, 3.	−0·0052	together = +0·0146.
,, 4.	+0·0198	
,, 5.	−0·0190	together = +0·0008.
,, 6.	+0·0198	

* *Comptes Rendus*, vol. lxxx., 1875, p. 976. Their apparatus was intended for use in the fateful ascent during which Crocé-Spinelli and Sinel lost their lives.

† *Annales de Chimie*, vol. xxvi., 1882, p. 222.

‡ *Annalen der Physik*, vol. xxiv., p. 570.

* *Annales de Chimie*, vol. x., 1844, p. 456.

† *Sitzber. der Wein. Acad.* (Math.-nat. Kl.), vol. xx., p. 189.

‡ *Zeitschr. fur Anal. Chem.*, vol. i., p. 3.

§ *Ibid.*, vol. v., p. 87.

‖ Of the pattern used by Voit in his smaller respiration apparatus (*Zeitschrift fur Biologie*, vol. xi., p. 157).

Experiment B.

20 litres of air driven through the flasks in sixty-four minutes.

Flask 1.	+0·2530	
„ 2.	−0·0014	
„ 3.	+0·0012	together = +0·0185.
„ 4.	+0·0173	
„ 5.	−0·0200	together = −0·0028.
„ 6.	+0·0172	

Experiment C.

50 litres of air were driven through in two hours thirty minutes. In this experiment flasks 5 and 6 were replaced by a Pettenkofer absorption tube 100 c.m. long, containing 40 c.c. of dilute baryta-water of known strength, through which the air was made to bubble.

Flask 1.	+0·5660	
„ 2.	+0·0048	
„ 3.	+0·0090	together = 0·0468.
„ 4.	+0·0378	

Baryta-water before experiment, 20 c.c. = 20·9 c.c. standard oxalic acid.*

Baryta-water after experiment, 20 c.c. = 20·9 c.c. standard oxalic acid.

Allowance for evaporation, 0·6 c.c.

∴ loss of alkalinity of baryta-water = 0·6 c.c. = 0·0006 grm. CO_2.

Experiment D.

50 litres of air were driven through in 1 hour 18 minutes. In this experiment the air-current, after passing through flask 4, was divided by means of a T-tube, and passed through two Pettenkofer tubes. The loss of water from these Pettenkofer tubes was determined by means of a sulphuric acid flask placed in the air-current beyond them. The moisture which had collected in the tubing connecting the Pettenkofer tubes and this absorption flask was washed into the flask by means of a current of dry air.

Flask 1.	+0·5205	
„ 2.	+0·0016	
„ 3.	+0·0398	together = 0·0754.
„ 4.	+0·0356	

Baryta-water before experiment, 20 c.c. = 20·9 c.c. standard oxalic.

Baryta-water after experiment, tube 1, 20 c.c. = 20·7 c.c. standard oxalic.

Baryta-water after experiment, tube 2, 20 c.c. = 20·9 c.c. standard oxalic.

Loss of water by evaporation, 0·5932.

∴ loss of alkalinity in tube 1 = 0·4 c.c. standard oxalic, and loss by evaporation in tubes 1 and 2 = 0·6 standard oxalic.

Together = 1 c.c. = 0·0010 grm. CO_2.

Experiment E.

80 litres driven through in 1 hour 5 minutes. Arrangement as in Experiment D, except that the air-current was divided between six Pettenkofer tubes. The baryta-water from the tubes was mixed in a covered vessel after the experiment and titrated.

Flask 1.	+0·8972	
„ 2.	+0·0204†	
„ 3.	−0·0290	together = +0·0408.
„ 4.	+0·0698	

Baryta-water before experiment ..	(1)	40 c.c. = 40·5 c.c.	standard	oxalic.
	(2)	„ = 40·7	„	„
	(3)	„ = 40·7	„	„
Mean		40 c.c. = 40·63	„	„
Baryta-water after experiment ..	(1)	40 c.c. = 40·5 c.c.	standard	oxalic
	(2)	„ = 40·4	„	„
	(3)	„ = 40·5	„	„
Mean		40 c.c. = 40·47	„	„

Water lost by evaporation = 1·165.

∴ loss of alkalinity (= 0·16 × 6) = 0·96 c.c. standard oxalic, and loss by evaporation = 1·17 c.c. standard oxalic.

Together = 2·13 c.c. = 0·00213 grm. CO_2.

In the majority of these experiments there is an apparent slight escape of moisture and CO_2 through the first sulphuric acid and soda-lime flasks. In experiment B, however, the test flasks, both for moisture and CO_2, show a diminution in weight. This suggested that the apparent escape might be explained by errors of weighing. Such an explanation does not, however, apply to the cases in which there was an apparent escape of CO_2 into the baryta water, and we at first thought that the diminution in alkalinity of the baryta-water was conclusive proof of escape of CO_2. It will, however, be shown later that the errors of experiment connected with Pettenkofer's method fully account for this apparent escape.

The results of these preliminary experiments at any rate showed that the gravimetric method might be used for the animal respiration apparatus. Such an apparatus was accordingly constructed.* The results of a number of test experiments made with it determined us to enter upon the present research, as they showed distinctly that the gravimetric method must be capable of giving much more accurate results than those quoted above.

(To be continued).

* 1 c.c. = 0·001000 grm. of CO_2.

† Flask 1 was probably spent.

* A full account of this apparatus will shortly be published. A preliminary paper on the subject was published in the *Proceedings of the Oxford University Junior Scientific Club* for October term, 1888.

† A Paper read before the Royal Society, May 2, 1889.

RESEARCHES IN THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.†

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C., Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C., Demonstrator of Chemistry, R.C.S.I.

(Continued from p. 234).

The Conditions which Affect the Freezing-points of Selenic Acid and Sulphuric Acid.

It has long been recognised that in order to determine the melting-point of a chemical compound with accuracy it is necessary, by crystallisation or other means, to obtain it in a pure condition. The necessity for such a precaution is well shown in the case of the oxides and acids of sulphur and selenium. An example taken from the former class of bodies is furnished by sulphuric anhydride. Up to a comparatively recent date great diversity of opinion prevailed regarding the melting-point of this substance until Weber showed that, as hitherto examined, it had usually contained a minute quantity of water, which had the effect of altering its melting-point, crystalline form, and other properties. Sulphuric acid supplies another instance of a similar effect. Its melting-point in the anhydrous condition is 10·5°, while that of the monohydrated acid is 8°; yet commercial sulphuric acid has usually been found to remain liquid above a temperature of −30° or −40°, and it is stated in some chemical works that by addition of a little water to the commercial acid its freezing-point has been lowered to −80°; but it is not mentioned whether this occurred in closed or in open vessels. A still more striking example of the influence of want of purity upon the melting-point is afforded by selenic acid. In the anhydrous state it melts at 58°, but

a slightly dilute acid, as we have found, was frozen only when a temperature of −51·5° was reached, showing a fall of 109·5°; and probably further dilution would be attended by a still greater reduction of the freezing-point. The depression of the freezing-point can be due only partly to superfusion, since the superfused anhydrous acid freezes at about 5°. The monohydrate present in the dilute acid therefore exerts an influence in lowering the freezing point of the anhydrous acid, and also its melting-point. An analogous action probably occurs in the case of some metallic salts, which, although without apparent chemical action upon each other, have a lower fusing-point when mixed than when heated separately. A consideration of the foregoing facts leads to the conclusion that *dilute selenic acid having a strength greater than 88·96 per cent contains the anhydrous and also the monohydrated acid existing in a superfused state, and exerting a solvent action upon each other.* In the case of sulphuric acid a similar action evidently occurs. The effects of agitation and of alteration of pressure upon the freezing-points of the above acids have already been referred to.

The Method Used in Freezing Selenic Acid.

Liquefied sulphur dioxide was poured into a thick glass tumbler, holding about half a litre, fitting into a somewhat wider and deeper cylindrical gas jar, which served to retain any of the dioxide splashed from the interior vessel, the whole being imbedded deeply in a considerable quantity of cotton wadding contained in a wooden box. A rapid current of air was driven through the sulphur dioxide, the air being first dried by means of sulphuric acid and then cooled by passing through a leaden worm surrounded by a mixture of salt and pounded ice, or, less effectively, sodium sulphate and hydrochloric acid. Any desired degree of cold within limits could easily be maintained by regulating the current. When the outside air was at 0° about half a kilogramme of sulphur dioxide was found sufficient for more than two hours' use, evaporation taking place but slowly at the low temperature reached, the latter, measured with an alcohol thermometer, falling below −50° C. In warmer weather nearly as low a temperature was obtainable, but consumption of the sulphur dioxide was much more rapid. No arrangement of freezing mixtures produced nearly so low degrees of cold as were attained in the above manner. Doubtless when a supply of dry snow is available, and the weather is very cold, so that the apparatus and materials used can be well cooled down previous to mixing, a very low temperature is obtainable by ordinary freezing mixtures, but those conditions are not often to be met with in these climates. On the other hand, sulphur dioxide is cheap and easily procurable and convenient when used in the manner described.

The Specific Gravities of the Higher Strengths of Selenic Acid.

The specific gravities of selenic acid for the higher strengths, taken in the liquid state at 15°, are given in the following table. The most concentrated acid, of 99·73* per cent strength, has been referred to when describing the preparation of the anhydrous acid; its specific gravity, 2·6083, was taken while in the superfused condition. The next acids down to 94·74 per cent were obtained by diluting that of 99·73 per cent. The acid having a strength of 93·70 per cent was obtained by heating dilute acid in a vacuum at 100°, and it supplied the following strengths down to 82·52 per cent by progressive dilution. That of 81·73 per cent was prepared by concentration on the water-bath, and the remaining four by dilution of the latter. Neither the acid heated in a vacuum, nor that which was kept on the water-bath, contained any trace of selenious acid.

* 99·73 per cent of selenic acid, acid sodium selenate, equivalent to 0·07 per cent of neutral sodium selenate, and 0·20 per cent of water (Se being = 78·87).

TABLE I.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·08	2·5993
98·68	2·5901
98·16	2·5790
97·37	2·5676
96·97	2·5595
96·16	2·5424
94·74	2·5105
93·70	2·4852
92·83	2·4534
91·59	2·4218
90·06	2·3863
89·20	2·3642
88·55	2·3402
87·34	2·3158
86·60	2·2946
85·67	2·2712
84·59	2·2463
83·82	2·2196
82·52	2·1878
81·73	2·1694
80·86	2·1438
79·99	2·1213
79·06	2·0940
73·43	1·9659

Table II. is calculated from Table I., and gives specific gravities interpolated for equal increments of strength. It will perhaps be found most convenient for purposes of calculation, and for showing the relation of the rate of increase of specific gravity to that of the strength.

TABLE II.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·50	2·6051
99·00	2·5975
98·50	2·5863
98·00	2·5767
97·50	2·5695
97·00	2·5601
96·00	2·5388
95·00	2·5163
94·00	2·4925
93·00	2·4596
92·00	2·4322
91·00	2·4081
90·00	2·3848
89·00	2·3568
88·00	2·3291
87·00	2·3061
86·00	2·2795
85·00	2·2558
84·00	2·2258
83·00	2·1946
82·00	2·1757
81·00	2·1479
80·00	2·1216
79·00	2·0922
73·50	1·9675

The rate of increase of specific gravity is not uniform for equal increments of strength. It diminishes as the strength increases, as in the case of sulphuric acid, but not regularly. The diminution is very marked at the highest strengths. When sulphuric acid has arrived at the greatest strength attainable by ebullition—98·66 per cent—its specific gravity is stated to decrease until the anhydrous acid, H_2SO_4, is reached. Selenic acid behaves dissimilarly in this respect; the increase of its specific gravity, although not uniform, is maintained throughout.

Berzelius (*Traité de Chimie*, 1830) mentions that selenic acid of 95·9 per cent strength has a specific gravity of 2·6.

Fabian gives 2·609 as the specific gravity of an acid of 94·9 per cent strength, and 2·627 for an acid of 97·4 per cent. It will be seen that these results do not agree, nor are they consistent with those we have obtained. If values for the strengths mentioned be calculated from the foregoing tables, an acid of 95·9 per cent will be found to have a specific gravity of 2·5366, while the specific gravities of 94·9 per cent and 97·4 per cent acids will be respectively 2·5141 and 2·5680, being less than those assigned above. Furthermore, the difference between the two specfiic gravities given by Fabian is much less than we find between two acids differing by 2·5 per cent. The most probable explanation of the discrepancy is that the acids which gave the above results contained sufficient selenium dioxide to raise their specific gravities appreciably. It may be shown that the effect of the development of selenium dioxide in selenic acid is to increase the specific gravity relatively to the acidity. In the acids above mentioned, selenium dioxide would exist as such, and not as selenious acid, owing to dissociation of the latter at a temperature below those at which the acids were formed, and the weak affinity for water possessed by the resulting dioxide. Clausnizer (Liebig's *Annalen der Chemie* (1879), 196, 265) gives the specific gravity of selenium dioxide at 15·3° as 3·9538. We have also recently taken its specific gravity, and are in a position to confirm his result. It is thus more than one and a half times as dense as the strongest selenic acid. C. Blarez (*Comptes Rendus* (1886), 103, 804—806) has examined the saturating power of selenious acid. He finds that it is monobasic with cochineal or methyl-orange. With litmus, it is monobasic to ammonia, lime, strontia, and baryta, but with soda or potash the litmus only becomes blue-violet when about 1·5 equivalents of alkali are added. We have obtained a like result with soda or potash and litmus. When one equivalent of the acid is saturated, there is a distinct change in the colour of the litmus, so that in the absence of other acids it might be used as an indicator for selenious acid. Taking 1·5 equivalent of alkali as the limit, the molecule of selenium dioxide in solution will have a less saturating power than that of selenic acid in the ratio of 2 : 1·5. This will be partly counterbalanced by the higher molecular weight of the latter, but the final effect of the substitution of selenium dioxide for selenic acid will be to reduce the acidity. A gravimetric method by which selenium dioxide would be oxidised and estimated as selenic acid, would also show a less acidity compared with the specific gravity than if the pure acid were used, but not to the same extent as when a volumetric process is employed for estimating the strength.

Erratum.—At p. 233, col. 2, paragraph 7 should read as follows, the words enclosed in brackets being inserted :—

"This acid commences to boil at 205°, the acid vapour given off being at first very weak, but it increases in strength with the rise in temperature. A more dilute acid [gives off water only until the temperature reaches 205°. Dilute sulphuric acid] is stated to behave in a similar manner, giving off nothing but water until the boiling-point reaches 205°—210°, at which temperature it has the strength of the monohydrated acid, H_2SO_4,H_2O."

(To be continued).

FATAL POISONING BY CARBON MONOXIDE.

By Prof. W. P. MASON.

In Troy, N.Y., on January 6, 1887, owing to a break in the street mains, a quantity of "Fuel Gas" (see analysis below) passed beneath the frozen crust of earth, and found its way into the adjoining houses. Three deaths, and many more or less serious illnesses, resulted.

The following points, from the testimony of the physicians who made the autopsis, are to be noted :—

The expressions of the deceased were placid. One victim, an old woman, was found seated in a chair holding her false teeth in her hand. The second, also a woman, lay upon the floor. The third, a man, sat upright on a lounge, his head reclining on his shoulder. The fire was burning in the stove, and the lamps were still burning on the table. When found, death had not been very recent, as "*rigor mortis*" was fully developed.

Very searching autopsis were made, with the result of finding nothing whatever abnormal, with the exception of the bright cherry-red colour of the tissues, and the vivid redness and lack of coagula in the blood.

Upon opening the chest cavity the physician bent forward and took one or two long whiffs for the purpose of determining the presence of any odour. Almost immediately he was seized with giddiness and great oppression in the epigastrium, so much so that he had to discontinue his work for half an hour. The effects did not finally wear off until after an interval of about twelve hours.

The painful oppression in the chest, the giddiness, and the subsequent headache experienced by this physician, call most forcibly to mind the symptoms described by Sir Humphry Davy, when he so rashly experimented upon himself with carbon monoxide.

A lawsuit naturally growing out of these cases of poisoning, I was called upon to give the chemical constituents found in the said "Fuel Gas," and the results are appended. I also experimented upon animal life with carbon monoxide mixed with air, obtaining results confirmatory of observations already made, that death usually takes place very quietly, although occasionally with convulsive movements. Chickens and rats were the two forms of life employed.

Blood, treated with carbon monoxide, I found to assume a bright red, almost carmine, colour, which did not alter on exposure to air for a number of days.

Finally, in February, 1888, a bottle of blood taken from the heart of one of the victims at the time of the autopsy, was submitted to me for examination. The bottle was closed with a tight cork. Although over a year old, and possessing strong odour of decomposition, the colour still remained of the brilliant, vivid red noted at the time of taking the specimen. Under the microscope but very few corpuscles remained to be seen, their structure having almost completely broken down.

Examination by the spectroscope revealed the two absorption bands near the line, characteristic of the presence of carbon monoxide in combination. These bands, although very like those indicative of oxy-hæmoglobin, may yet be readily distinguished by their location only, particularly if a sample of blood artificially treated with carbon monoxide be at hand for purposes of comparison.

The space between the bands is, moreover, much less clearly lighted than in the case of oxygenated blood. As a confirmatory test, the blood under examination was treated with solid potassium sulphide, and the absorption bands found unchanged thereby—the bands of oxy-hæmoglobin, as is well known, change under such treatment to the single dark band midway between the positions of the former ones.

What is of special interest in this case is the ready detection of carbon monoxide in the blood after so long an interval of time.

Ar the present moment, nearly two years from the date of the accident, the blood still retains the characteristics noticed when first examined.

The analysis of the Fuel Gas by volume is :—

CO_2	5·0 per cent
O	0·5 ,,
CO	37·5 ,,
CH_4	0·9 ,,
H	48·0 ,,
N	7·1 ,,

Such gas supplied to consumers is practically odourless. —*Journal of the American Chemical Society*, Vol. x., No. 9.

ESTIMATION OF TEA TANNIN.*

By JOHN TSAWOO WHITE.

So many and so various are the proposed methods of tannin-estimation, that in trying some samples of cutch or catechu it became necessary and important to choose a method of estimation. Therefore a reliable method, new or old, was necessary to be tried experimentally.

In looking round for a substance that would serve as a standard, the search chanced upon a sample of tea, commercially named Assam Pekoe Souchoung. The tannin in it was first determined by Lowenthal's method, acknowledged to be the best. Assuming with Rochleder that tea tannin is identical with quercitannic acid, and employing Neubauer and Oser's factor for this acid, it gave 11·9 per cent tannin. I must, however, say that the end reaction was not quite distinct, at least to my eyes. A solution, 4 grms. per litre, was used in all experiments; it was prepared by boiling 2 grms. of tea with a little less than 500 c.c. water for an hour, allowed to cool, diluted up to the mark, and filtered.

Then I tried precipitating tannin with a standard solution of acidified lead acetate. An excess of lead solution was used, and the excess determined in the filtrate. But as the composition of the lead precipitate is unknown, no results were obtained by these experiments. The acetic acid was added to keep up gallic acid. A solution containing enough of acetic acid to keep up a 4 grms. per litre solution of gallic acid from not precipitating, at first gave, however, a precipitate on being allowed to stand for a few hours.

My next trial was with ammoniacal zinc acetate, a reagent so characteristic and therefore so full of promise, a reagent used by Barbieri, Carpene, and Ferreil. A solution containing 100 grms. ZnO per litre was prepared. On adding ammonia to the zinc acetate there is a point where the first formed precipitate is almost entirely redissolved; 100 c.c. strong ammonia are now added, and then diluted to the litre mark: this solution gives a precipitate on diluting with water. Instead of dissolving the zinc tannate in sulphuric acid and oxidising it with $KMnO_4$, the precipitate was dried at 100° C, and the tannin calculated from its organic matter. This method I saw the late Dr. Romanis use occasionally; I do not know if it has been used by others. Zinc tannate is soluble in 14,600 parts of water at 21° C; and it is more insoluble in hot water—a single experiment gave its solubility as 1 part in 60,500 parts of water at 90° C. 100 c.c. of tea solution is precipitated in the cold with 10 c.c. zinc solution, allowed to stand an hour or two, filtered, and washed with hot water; boiling or allowing it to stand long will deposit an adherent coating of ZnO on the sides of the beaker, which is difficult to remove.

To avoid the troublesome and often annoying use of weighed filter-paper, the following method was adopted:—

After washing, the bulk of the undried precipitate is easily removed from within the folds of the filter: when dried, the precipitate sticks to the filter. The tannin is determined in this. Then the remainder of the tannate is ignited, and assuming that the precipitate is uniform, the total tannin is easily calculated. It is an advantage to use hydrochloric and hydrofluoric treated filter-papers like Schleicher and Schüll's; it will save correction for filter-ash. One experiment gave 19 per cent tannin, the tannate containing 54·53 per cent ZnO. Zinc tannate is more soluble in ammoniacal water: I did not try its solubility. The evidence of its solution may be seen by adding ammonia to some zinc tannate in suspension in water. The colour of the solution, previously slightly yellow, becomes at once dark coloured.

I next tried the tannin in 100 c.c. tea solution with the addition of 10 c.c. strong ammonia, often adding zinc acetate to make the strength equal to that of the zinc solution. The tannin was now 9·8 per cent, showing great solvent action, and the tannate contained 36·63 per cent ZnO. Instead of ammonia, 5 c.c. saturated solution of ammonium chloride was next added to prevent zinc oxide precipitating along with the tannate. The tannin was now 15·6 per cent, the tannate containing 34·02 per cent MO. This last and probably the best determination may be accepted as the amount of tannin obtained by this method. Before these experiments were tried I dissolved the tannate in acetic acid, precipitated the zinc with H_2S, evaporated the filtrate, and weighed the residue as pure tannin. Fairly constant, but low, results were obtained, viz., 8·2 per cent, 8·9 per cent, and 8·4 per cent tannin.

The evaporation values of a tannin solution evaporated with alcohol, with acetic acid, and with formic acid, were appreciably variable.

Zinc tannate is insoluble in methylated spirits, but it is difficult to wash with spirit.

As tannin is removed from solution by digesting with copper and zinc oxides, I tried digesting the tea solution with the dried oxides. The tea gave 31·9 per cent extract. The amount retained by the oxides was then determined by evaporation loss. Copper oxide acts more readily than zinc oxide. Alumina also removes tannin from its solution. As the moist oxide and hydrate may act more easily than when dry, some copper oxide and aluminium hydroxide were prepared by precipitation, and the tea solution was treated with copper oxide and aluminium hydrate in suspension in water. Copper oxide removed 18·9 per cent, and aluminium hydroxide 19·9 per cent and 19·6 per cent; thus a little over one half of the extract is absorbed.

Tannin is precipitated by aluminium acetate. A solution of aluminium acetate was prepared by digesting the hydroxide in 1 litre of water containing 100 c.c. acetic acid for a week, then diluting to 4 litres and filtering. The solution contains 2·7 grms. Al_2O_3 per litre. I find the acetic acid I use to contain 30 per cent anhydrous acid by titrating with potash and phenolphthalein. 100 c.c. of the tea solution are precipitated with 50 c.c. of the aluminium solution, filtered after an hour; the supernatant liquid is not always clear. It is washed with hot water; the precipitate washes easily. The tannin is then calculated from the loss on ignition after having dried and weighed it, the drying being done at 100° C. Three experiments gave 16·9 per cent, 15·3 per cent, and 16·4 per cent tannin, the tannate containing respectively 23·79 per cent, 26·57 per cent, and 20·17 per cent Al_2O_3. Gallic acid is not at first precipitated by aluminium acetate solution, but gives a blue colour due to traces of iron in the reagent. After some hours, however, a precipitate falls. I tried one experiment with gallic acid, a preparation of Messrs. Mottershead and Co. Only 77 per cent of the gallic acid is precipitated, the gallate containing 33·2 per cent Al_2O_3. The filtrate gave an intense blue colouration with ferric chloride. A trial with a sample of tannin, obtained from the Rangoon Medical Hall, with aluminium acetate gave the amount of tannin as 96·6 per cent, the tannate containing 25·07 per cent Al_2O_3.

Aluminium gallate dissolves easily in acetic acid. A solution of gallic acid, 4 grms. per litre, gave no precipitate with aluminium acetate containing additional acid of 50 c.c. per litre, even after standing over night—over fifteen hours. Tannin solution of the same strength is immediately precipitated. The tannate, however, dissolves when strongly acidified. 100 c.c. tea solution treated with 50 c.c. of aluminum acetate containing 50 c.c. additional acetic acid per litre, gave a slightly different result. The supernatant solution was clear, and it gave 13·5 per cent tannin, the tannate containing 14·5

* Contribution from the Laboratory of the Chemical Examiner to Government, Burma.

per cent Al_2O_3. This is the latest determination of tea tannin with aluminium acetate. An advantage in using this reagent is this: that platinum crucibles may be used.

I intend to continue my experiments on other tannins and tannin containing bodies.

Aluminium acetate, like ferric acetate, the reagent of Handtke, might be found unsuited for some tannins. But may not tannins unprecipitated by aluminium acetate be unsuitable for tanning?

The above results are communicated as they may be of independent value and interest.

Rangoon, April 19, 1889.

THE TESTING OF LOGWOOD EXTRACTS.*

By T. C. PALMER.

The author remarked that he wished to call particular attention to the statement in his paper, that under the conditions of the test for strength of logwood extracts, with which the paper dealt, the compounds of tannin and copper oxide were nearly or quite colourless. This difference in behaviour between tannin and hæmatine was the more remarkable, since in many other respects the latter acts precisely as a tannin. This is even true with respect to its action on hide powder. An attempt to estimate the tannin in a pure extract of logwood, by means of filtration through powdered hide, had resulted in an apparent showing of twenty per cent of tannin, which loss was evidently due to an absorption of the hæmatine by the hide. In fact, the attraction of the hide for the colouring matter is quite as strong as it is for tannin. He here showed a column of hide powder deeply coloured by the passage through it of a very dilute clear solution of logwood.

The author also made some preliminary remarks on the faultiness of the tannin process of Hammer, as modified by Procter, giving data that show the amount of soluble matter in hide powder to depend very largely on the time the water is in contact with the hide, *i.e.*, in the rate of percolation. The hide powder, made by Schuchardt, gave to water an extract that left a residue on evaporation, ranging in amount, easily oxidisable, soluble in water, and with many of the reactions of the so-called coriin. The one fact above all that showed the faultiness of the process of Procter was that this residue, when re-dissolved in water, *was precipitated on addition of tannin solution*. Thus while the amount soluble in water could be only roughly estimated, the amount dissolved out by the tannin solution was simply unknowable, since at the top of the column, where the tannin is in abundance, there would be no dissolving out of the coriin, but as the liquor trickled down, losing tannin, it would dissolve more and more. The author stated that he expected shortly to bring before the Section his method of obviating this difficulty, retaining hide powder as the absorbent of tannin, but obtaining the tannin strength of the solution before and after filtration by an expedient that rendered evaporation of solutions or specific gravity determinations unnecessary.

ON THE COMPOUND $C_{21}Cl_{26}$.*

By EDGAR F. SMITH and HARRY F. KELLER.

In 1876† one of us (S.) described a compound containing only carbon and chlorine. It was obtained by the exhaustive chlorination of toluene exposed to sunlight, first at the boiling temperature and then in the cold. Several analyses of the purified product showed the presence of 21·40 per cent carbon and 78·6 chlorine. The only solvent employed at the time was chloroform, and from such a solution crystals, measuring one-half inch in length and one-fourth inch in breadth, were obtained. The forms were apparently orthorhombic. The melting-point, taken after each of a series of re-crystallisations, remained constant at 152°—153° C. To this rather interesting derivative the improbable formula $C_{21}Cl_{26}$ was ascribed. Nascent hydrogen acted with difficulty upon it. After an exposure of two months to the influence of zinc and sulphuric acid it was scarcely changed, inasmuch as an analysis of the product gave 21·69 per cent carbon, 77·76 per cent chlorine, and 1 per cent hydrogen.

Nothing further was done with the compound until about five years later, when a portion of it was treated in a sealed tube with an excess of aniline (*Am. Chem. Jour.*, vol. i., p. 150). By this treatment a base was formed, melting at 230° C. Its hydrochloric acid salt was analysed.

Crystals of the original compound, in its purest condition, were preserved for twelve years without undergoing any visible alteration, and it was but natural that we should be surprised, on fusing some of this same material, to find it melting at 101° C. This melting-point remained constant, even after re-crystallisation from pure chloroform. On heating a portion of the substance in a test-tube, we observed that hydrochloric acid gas was evolved. A combustion gave 22·8 per cent carbon and 2·2 per cent hydrogen. A vapour density determination was carried out, but, as we had evidence of decomposition, we place no reliance on the result. Every possible precaution was observed in the combustion, in order that we might arrive at the true hydrogen percentage, and that given above would indicate but slight change from the original constitution. Work is now being prosecuted with a view of obtaining the carbon chloride, when it is proposed to pay especial attention to the solution of its molecular formula and to the study of some of its derivatives. We therefore request those who may have entertained the idea of investigating this compound to postpone their work, and leave the field to us, at least, for a few months.

ON THE RE-DETERMINATION OF THE ATOMIC WEIGHT OF PALLADIUM.*

By Dr. E. H. KEISER.

The atomic weight of palladium has not been determined very carefully. The only data for the calculation of this constant, at the present time, are two analyses of the double chloride of palladium and potassium made by Berzelius in 1828. These two analyses do not agree very well. The first one gives 105·7, and the second one 106·2 for the atomic weight of palladium.

For the purpose of re-determining this atomic weight, metallic palladium in the form of foil was dissolved in aqua regia and the solution evaporated to dryness. The palladium chloride was then dissolved in dilute hydrochloric acid and the solution was filtered. Ammonia was added to the filtrate until the precipitate, which at first formed, was re-dissolved. After filtering the solution again, to remove any traces of ferric hydroxide, the filtrate was saturated with hydrochloric acid gas. The palladium is thus precipitated as palladium-di-ammonium chloride, $Pd(NH_3Cl)_2$, a yellow crystalline compound which is insoluble in water and acids, but which is readily soluble in dilute ammonia.

The yellow precipitate was re-dissolved in dilute

* Chemical Section of the *Journal of the Franklin Institute*, April, 1889.

† "Dissertation." Goettingen, 1876; *Jahresbericht*, 1877, p. 421; *Am. Phil. Soc.*, xvii., p. 29.

* Chemical Section of the *Journal o the Franklin Institute*, April, 1889.

ammonia, and the solution was filtered. If any rhodium had been present in the original sample of metallic palladium, it would have been separated by this process, because the rhodium di-ammonium chloride is insoluble in dilute ammonia. The filtrate was thereupon treated with hydrochloric acid and the palladium di-ammonium chloride thus precipitated was thoroughly washed with distilled water until all ammonium chloride was removed. The compound was carefully dried over sulphuric acid in a partial vacuum.

The compound was analysed by weighing off portions in platinum boats and heating up in a current of pure hydrogen. At a low temperature the yellow compound absorbs hydrogen, metallic palladium and ammonium chloride being formed.

$$Pd(NH_3Cl)_2 + H_2 = Pd + 2NH_4Cl.$$

On raising the heat the ammonium chloride is completely volatilised, and spongy palladium remains behind. After the boat and its contents had cooled off somewhat, the hydrogen stream was replaced by one of dry air, and the boat was allowed to cool off completely in the air. By this means it was possible to avoid the retention of hydrogen by the palladium, and as the hydrogen stream was not displaced by air until the temperature of the palladium had fallen considerably below a low red heat, it was not possible that palladium oxide should have been formed.

Determination of Atomic Weight of Palladium.

I.—By ignition of $PdN_2H_6Cl_2$ in current of hydrogen.

No.	Weight of Substance.	Weight of Palladium.	Atomic Weight.
1.	0·83260	0·41965	106·459
2.	1·72635	0·86992	106·410
3.	1·40280	0·70670	106·355
4.	1·57940	0·79562	106·342
5.	1·89895	0·95650	106·321
6.	1·48065	0·74570	106·292
7.	1·56015	0·78585	106·322
8.	1·82658	0·92003	106·317
9.	2·40125	1·20970	106·355
10.	1·10400	0·55629	106·400
11.	0·93310	0·47010	106·366
Total ..	16·74583	8·43606	[106·3520]

Atomic weight = 106·35 H = 1· Maximum = 106·459
N = 14·01 Minimum = 106·292
Cl = 35·37 Difference = ·167
Atomic weight = 106·62, when O = 16.

The foregoing table contains the results of all the determinations that were made.

The investigation will be continued. It is intended to make a series of determinations by means of other palladium compounds.

NOTICES OF BOOKS.

A Dictionary of Explosives. By Major J. P. Cundill, R.A. Chatham: Royal Engineers' Institute. London: Hamilton, Adams, and Co.

The first point which must strike chemists and engineers in examining this eminently practical compilation is the multitude of explosives which have been suggested, patented, and often brought into use. We are no less struck by the absurdity of the names of some of these compounds or mixtures, and by the evident identity of many regarded as distinct by their inventors. The same idea, as Major Cundill remarks, has been patented and re-patented, and we may, perhaps, yet find a crop of litigation springing up not less luxuriant than that which occurred in connection with magenta.

The list of explosives practically used in this country is very limited. The author enumerates as such gunpowder, gun-cotton under various names, dynamite No. 1, blasting-gelatin, and gelatin dynamites. These two compounds are often confounded. Blasting-gelatin is a combination of nitro-glycerin and gun-cotton. Gelatin-dynamite is a thin blasting-gelatin mixed with nitrates, cotton, or charcoal.

We find in this work mention made of delusive experiments performed by manufacturers and their representatives to convince consumers or local authorities of the safety of their products. It is sometimes said that an explosive will burn away without explosion, and this may be true under certain circumstances. Thus, if a small quantity of gun-cotton is kindled or thrown into a fire it burns fiercely but quietly; yet if a fire breaks out in a magazine, part of the bulk having its temperature gradually raised reaches a point at which it explodes as destructively as if fired with a detonator. Dynamite may also be safely burnt in its ordinary unfrozen condition, but if it is gradually warmed in an oven or on a shovel over a fire, the result is generally a verdict of "Accidental Death." Major Cundill very justly says that in such cases the verdict should be suicide or manslaughter, as the case may be. The caution is also given that the compound which bears a blow without exploding may be made to detonate if previously heated. Attention is called to the effects of a glancing blow, combining percussion and friction. Such blows are likely to occur in charging a bore-hole, and they are far more effective than a much heavier blow given directly. Wearers or users of celluloid—that variety, at least, which consists largely of gun-cotton—may feel interested to learn that when heated it may be exploded by a shock.

The author classifies explosives in eight groups: gunpowder, ordinarily so-called, nitrate mixtures other than gunpowder, chlorate mixtures, nitro-compounds containing nitro-glycerin, nitro-compounds not containing nitro-glycerin, explosives in which picric acid or a picrate is a leading constituent, explosives of the Sprengel type, the essential feature of which is the admixture of a combustible with an oxidising agent, at the moment of or immediately preceding use, the constituents being non-explosive if taken separately, and lastly, miscellaneous explosives.

In a paragraph explaining the distinction between military and civil explosives we notice with profound regret a sentence which is perfectly true, but which may suggest to evil-disposed persons means for the most serious mischief.

The chlorated mixtures are very justly declared unsafe. This objection has been forcibly and distinctly put by Dr. Dupré, F.R.S.; Eissler and Berthelot concur in this opinion, and Major Cundill pronounces some of the compounds which he enumerates under this head to be "more or less dangerous haphazard mixtures." Some of them, *e.g.*, Augendre's "white powder," are capable of exploding even in the absence of one of the ingredients.

Melinite is mentioned, but its composition, not having transpired, is not given. It contains picric acid, and in the author's opinion it much resembles Turpin's explosive (Spec. No. 15,089, 1885). He thinks that nitro-benzol or some analogous material is also used. "A portion of the explosive as used to fill shells is said to be termed cresilite. Kresylic acid corresponds to carbolic acid, but contains the hypothetical radicle kresyle (C_7H_7) in place of phenyle (C_6H_5)."

The Sprengel explosives (Spec. No. 2642, 1871), and *Journal of the Chemical Society*, August and September, 1873) are a very interesting class of bodies. Whilst their power cannot be disputed, the circumstance that they have to be made on the spot forms not only a legal but a practical barrier to their extensive use.

In conclusion the author gives certain "words of

caution" which, if attended to, would save much mischief:—

"The function of an explosive is to explode. Remember this in dealing with them. If an explosive is described as absolutely safe under all circumstances, do not treat it as some people treat a big dog, and try how much it will stand. There is no explosive, within my knowledge, in practical use which, when exploded in a confined space, does not give off noxious or deleterious gases. Do not expect the same class of explosive to do every variety of work. Different classes have their different functions. If using an explosive with which special instructions are issued, it is wiser to read them before an accident happens than to have to refer to them afterwards, to see if they are not issued for some good reason. Do not apply the sense of taste to explosives. In the case of nitro-glycerin and nitro-benzol compounds the consequences may be unpleasant."

Major Cundill's work will prove exceedingly valuable to all who manufacture, use, or study explosives.

Thirtieth Annual Report of the Inspector of Milk and Vinegar. From Jan. 1st to Dec. 31st, 1888. Boston: Rockwell and Churchill, City Printers.

The Inspector finds himself able to assert that in no large city in the world is the adulteration of milk suppressed to the degree which now prevails in Boston. This result reflects the greater credit upon the authorities since we are told that a few years ago 60 per cent of all samples were below the standard. For the year 1885 the percentage of poor samples was 30·64; for 1886, 18·55; for 1887, 12·54; and for 1888 only, 8·49. Every dealer is liable to have his milk tested on any day (Sundays included), and at any hour. The samples inspected, according to their merit, are either "passed" as good, "warned," or, in the worst cases, "reported" for prosecution. Of the 108 cases disposed of during the year, 87 cases were finally decided in favour of the prosecution. *Two* appeals seem to be allowed, firstly to the Superior Court, and secondly to the Supreme Court.

A preliminary examination of the samples is made by means of Feser's lactoscope, the results turning on the greater or less opacity of the sample, and by Pile's hydrometer, with correction for temperature. Instead of warming or cooling the milk to some standard degree, the sp. gr. is taken at any temperature, and then reduced to standard by calculation, the tables for which are here given.

If the results of this preliminary examination are condemnatory or doubtful, a chemical analysis follows, the points determined being total solids, solids not fat, fat, ash, milk-sugar (ascertained by means of the Ventzke-Scheibler polariscope), and albumenoids.

For the detection of annatto two methods are in use. The first is applicable to fresh, sweet milk only, and is as follows:—100 c.c. of the sample, rendered alkaline by the addition of 5 c.c. of solution of sodium carbonate (1 part in three of water), are poured into a glass jar, 1½ inches in diameter and 4—5 inches high. In this jar is placed a strip of white filter-paper (Schleicher and Schüll's No. 568) 5½ inches long and ½ inch wide. The jar is set aside for twelve hours in the dark, the paper is withdrawn and washed in running water, when, if annatto be present, and if, while still moist, it is dipped in a solution of stannous chloride, it appears of a pale salmon colour. If the milk is sour the colouring-matter of the annatto is precipitated, and escapes detection. The pink colour may be brought back to the original salmon tint by immersing the slip in a dilute solution of sodium carbonate. It is then well washed, dried in the cold, and further tested with dilute sulphuric acid (2 parts acid and 1 part water), which produces a bluish colour with annatto.

The second method, which is applicable to sour or stale milks, sets out with the precipitation of the caseine. Four fluid ozs. milk are coagulated in heat with a few drops of acetic acid. The colouring matter goes down in the caseine, which is then freed from serum by pressing and straining and ground up in a porcelain mortar with a fluid oz. of ether added in small portions, and is finally decanted off into a small globular separating apparatus having a stopper at the top and a stop-cock at the lower part. From 5 to 10 c.c. of dilute caustic lye (1 part sodium hydroxide in 100 of water) are added, and the whole is well shaken up. When the liquids have separated, the lower stratum of liquid, holding the annatto in solution, is drawn off into two small porcelain capsules of such size that the depth of the liquid in each may not exceed ¼ inch. In each capsule is then placed a disc of strong filter-paper, ½ in diameter, which are let stand for twelve hours in the dark and are then taken out and washed in fresh water, and may then be tested with stannous chloride or sulphuric acid as in the first method.

The detection of caramel, boracic acid, and salicylic acid and the microscopic examination of milk have also engaged the attention of the Inspector.

The oleomargarine question comes here to the front. The Inspector agrees with most eminent authorities that margarine is not injurious, and that it is objectionable only when sold under false names or when used in mixture with genuine butter. The only weak point in the law of Massachusetts on this subject seems to be that the name "butterine" is still tolerated.

Another question is the artificial colouration of butter, by which it is rendered possible to mix up different makes, good, bad, and indifferent, without the mixture being at once manifest to the eye of the purchaser. The colouring matter used is annatto, extracted by boiling or steeping in cotton-oil, linseed-oil, or whichever other oil happens to be the cheapest, and thus a considerable quantity of foreign fat is introduced into the butter. The manufacturers of these butter-colours—the names of whom are given boldly—assert that every gallon of their concoction used will increase the weight of the butter used by 8 lbs. The report contends—in our opinion with full justice—that the colouring of milk, butter, and margarine should alike be prohibited as opening the door for frauds indefinite in number.

On vinegar little is here said. During the last four years the percentage of poor vinegars sampled in Boston has fallen from 38·00 to 20·60 per cent. The author points out the distinguishing characters of cider-vinegar, which, when genuine, is not inferior to the white wine vinegar of France—now become rare—or to English sugar vinegars, and has an aroma never to be met with in alcohol or malt vinegars.

CORRESPONDENCE.

ALKARSIN.

To the Editor of the Chemical News.

Sir,—I find that by distilling chloride of acetyl, which is easily obtained by the distillation of concentrated hydrochloric with glacial acetic acid—

$$(HCl + C_2H_4O_2 = C_2H_3OCl + H_2O),$$

with an alloy of equal parts of zinc and arsenic, Zn_3As_2, an oily and fetid alkarsin is obtained, an acetide of arsenic. This liquid has an odour similar to arseniuretted hydrogen gas and acetic acid mixed, and seems to be decomposed by water or moisture into those two substances. If this be the case, therefore, the vapours of this alkarsin will act as deadly poison. When *I* made it, it did not fume or take fire in the air like ordinary alkarsin, viz., the mixture of kakodyle and its products of oxidation.

The alkarsin that I have discovered is merely an acet*ide* of arsenic, because the last part of the formula will not be O_2, as in other acetates. It may, however, combine with oxygen to form the *acetate*.—I am, &c.,

G. W. Blythe, M.P.S.

5, Alderley Road, Hoylake, Cheshire.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 18, May 7, 1889.

On the Origin of Bronze, and on the Sceptre of Pepi I., King of Egypt. — M. Berthelot.—In view of the comparative rarity of tin, the author agrees with the opinion of many archæologists that the use of pure copper must have preceded that of bronze. The sceptre of Pepi I., preserved in the British Museum, dates back to 3500—4000 years B.C. It is a small hollow cylinder of copper, covered with hieroglyphics. Through the intervention of the French ambassador M. Berthelot has obtained 0·0248 grm. of filings from the interior of the cylinder, which, on analysis, proved to be pure copper, free from tin and zinc, but containing a doubtful trace of lead. M. Berthelot thinks that the introduction of bronze does not date back beyond fifty to sixty centuries B.C.

On the Thionic Series. Action of Alkalies.—M. Berthelot.—The general theory of condensed anhydrides gives an exact explanation, at once chemical and thermochemical, of the constitution, the conditions of reaction, and the transformations of the thionic compounds. This applies equally to the metaphosphoric and pyrophosphoric acids, compounds condensed with loss as to their capacity of saturation compared with the normal tribasic phosphoric acid.

Researches on the Application of the Measure of Rotatory Power to the Study of the Compounds formed by the Action of Neutral Magnesium and Lithium Molybdates upon Solutions of Tartaric Acid.—D. Gernez.—The simplest combinations produced in aqueous solution by tartaric acid, and the neutral molybdates and tungstates which correspond to a maximum rotatory power, are formed by the union of the acid to the salt molecule to molecule.

The Atomic Weight of Ruthenium.—A. Joly.—Assuming O = 15·960 the author finds Ru = 101·49. Ruthenium has been freed from osmium, the atomic weight of which (191 according to the latest determinations of Seubert) is nearly double.

The Manganese Oxides obtained in the Moist Way.—A. Gorgen.—Hydrated manganous oxide, held in suspension in a mother-liquor containing an excess of manganese salt and submitted to the action of air, produces saturated manganite, $MnO_2,2MnO$, combined with variable quantities of water. Hydrated manganous oxide in alkaline liquors absorbs larger proportions of oxygen. On this fact depends the process of regeneration of oxides of manganese, as proposed by Weldon.

On Oxycinchonine-α.—E. Jungfleisch and E. Lèger.—This compound crystallises out of alcohol in colourless flattened prisms. It is insoluble in water but readily soluble in dilute alcohol and acetone, and more abundantly in strong alcohol, benzene, and chloroform. If saline solutions are not fluorescent they are precipitated by ammonia, but the precipitate re-dissolves in excess. It is isomeric with homoquinine, apoquinine, and apoquinidine, as well as with the oxycinchonines of Schutzenberger and Strecker.

The Alcoholic Fermentation of the Juice of the Sugar-cane.—V. Marcano.—The crude cane-spirit differs from other industrial alcohols by the presence of notable quantities of methylic alcohol, by the absence of the higher alcohols, and by the presence of an acid, *sui generis*.

Action of Zinc Chloride upon Isobutylic Alcohol in Presence of Hydrochloric Acid. Part of Isobutyl Chloride. Properties of Polybutylene.—MM. Malbot and Gentil.—Not adapted for useful abstraction.

The Determination of Organic Nitrogen by the Kjeldahl Process.—E. Aubin and L. Alla.—The authors prefer the Kjeldahl process to that of Will and Varrentrapp on the following grounds:—The dryness of the matter to be analysed. Many agricultural substances contain 15 to 40 per cent of moisture, and on mixing it with soda-lime there is sometimes an escape of ammonia. The liquid or pastey state is also inconvenient, as milk, beer, urine, drainings of dunghills, &c. The low sp. gr. of certain industrial waste and their hygroscopic quality. The heterogeneous character of certain materials; the difficulty of pulverisation. In the Kjeldahl process these properties do not interfere.

On an Artificial Silk.—M. de Chardonnet.—The author forms a nitrocellulose, dissolves it in a mixture of alcohol and ether, removes a portion of the nitrogen by immersion in nitric acid at sp. gr. 1·32 at a temperature falling from 35° to 25°. It is said to take up colours like natural silk.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 5.

Disposal of Refuse by Irrigation or Removal.—E. Reichardt.—The author, whilst advocating irrigation, admits that considerable quantities of potash and nitrogen are carried off into the rivers. For the disinfection of manure-heaps he recommends peat litter.

The Transformation of Nitrates in the Soil.—M. Berthelot.—From the *Comptes Rendus*.

The Production of Farmyard Manure.—A. Müntz and Ch. Girard (*Annales Agronomiques*).—The experiments relate principally to sheep. The authors find that a litter of earth retains the nitrogen of the excreta of these animals considerably better than does straw. Of 23·01 kilos. of nitrogen supplied to the sheep in their food (a straw litter being used) 1·67 kilos. were retained in the bodies, 8·90 were secured in the manure, and 12·44 (=51 per cent) were lost. P. P. Dehérain considers that had the authors used a larger proportion of straw the loss would have been smaller.

Manurial Experiments Conducted at the Pennsylvania State College.—W. Frear.—From the *Agricultural Bulletin of the Pennsylvania State College*, No. 14.

Influence of Manures on the Composition of Barley.—M. Krandauer (*Hopfenzeitung*).—The nitrogenous manure did not cause any marked increase in the nitrogen of the barley.

The Influence of Salt on the Digestibility of Protein in Various Articles of Cattle-food.—Prof. Sievert.—The addition of common salt appears to have no effect.

Variations in the Composition of Milk.—Harald Faber (*Tidskrift for Landökonomi*).—(See p. 253).

Influence of Petroleum-Steep upon the Germination of Maize.—Prof. Gustav Wilhelm (*Oest. Land. Wochenblatt.*—If the seed is steeped in petroleum germination is, and the growth of the plants is rather, delayed, and a smaller percentage of the seeds come up. But the injury is not so great as to necessitate the disuse of this experiment where the attacks of vermin are to be expected.

Researches on Inosite.—L. Maquenne.—From the *Bulletin de la Société Chimique.*

The Rational Feeding of Horses.—Prof. E. Wolff, Prof. Seiglin, and Dr. C. Riess.—At the conclusion of a long report on the experiments conducted in Paris in 1886-87 it is admitted that the question of the nutritive value of cellulose is not decided.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Molecular Weight.—Will some reader supply an answer to the following:—Explain how it is possible to determine the molecular weight of a substance by its influence in lowering the melting-point of a solvent.—S. J.

Viscous Liquids.—All viscous liquids, as far as I can make out, the fluidity being increased by increase of temperature, vary considerably in viscosity with ordinary variations of temperature. I shall be grateful to learn where, if possible, I may find a record of any observations on this subject, and whether there exists such a thing as a tolerably viscous liquid, which is but slightly affected by ordinary variations of temperature.—R. Snowdon.

MEETINGS FOR THE WEEK.

Monday, June 3rd.—Society of Chemical Industry, 8. "Naphthalin Derivatives of Technical Importance," by W. P. Wynne. "Purification of Alcohol by means of Hydrocarbon Oils," by Dr. W. S. Squire.

—— Royal Institution, 5. General Monthly Meeting.

Tuesday, 4th.—The "Faraday Lecture," by Prof. Mendeleeff, will be delivered in the Theatre of the Royal Institution, Albemarle Street, at 8.30 p.m. (Fellows of the Chemical Society desiring extra tickets for ladies or gentlemen are requested to apply to the Secretary).

—— Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.

Wednesday, 5th.—Geological, 8.

Thursday, 6th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.

—— Royal, 4.30.

—— Chemical, 8. "Experimental Researches on the Periodic Law," by Dr. B. Brauner. "The Amylodextrin of W. Naegali," by H. T. Brown and G. H. Morris. "The Determination of the Molecular Weights of the Carbohydrates (Part II.)," by H. T. Brown and G. H. Morris. "Researches on Silicon Compounds (Part IV.)," by Prof. Emerson Reynolds, F.R.S. "The Isomerism of the Alkyl Derivatives of Mixed Diazoamido Compounds," by Prof. Meldola and F. W. Streatfeild. "The Atomic Weight of Zinc," by Dr. Gladstone and W. Hibbert. "The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water," by R. Warington, F.R.S. "The Product of the Action of Sulphur on Resin," by G. H. Morris.

Friday, 7th.—Royal Institution, 9. "Recent Researches into the Origin and Age of the Highlands of Scotland and the West of Ireland," by Archibald Geikie, F.R.S.

—— Geologists' Association, 8.

Saturday, 8th.—Royal Institution, 3. "Idealism and Experience in Philosophy and Literature," by Prof. W. Knight.

—— Physical, 3. "On a Method of Suppressing Sparking in Electric Currents," by Prof. S. P. Thompson, D.Sc. "On a Shunt Transformer," by E. W. Smith. "Notes on Geometrical Optics:—(1) On the Deduction of the Elementary Theory of Mirrors and Lenses from Wave Principles; (2) On a Dioptric Spherometer; (3) On the Formula of the Lenticular Mirror; (4) On the Use of the Focal Circle in Mirror and Lens' Problems," by Prof. S. P. Thompson, D.Sc. "On the Use of the Biquartz," by A. W. Ward.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1541.

RESEARCHES IN THE CHEMISTRY OF SELENIC ACID AND OTHER SELENIUM COMPOUNDS.*

By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C.,
Professor of Chemistry and Hygiene, R.C.S.I.;
and JOHN MACALLAN, F.I.C.,
Demonstrator of Chemistry, R.C.S.I.

(Concluded from p. 260).

The Action of Heat upon Selenic Acid.

Action of Heat in a Vacuum.—The effect of heating dilute selenic acid in a vacuum up to 180° has already been described—dilute acid distils until that temperature is reached, when the anhydrous acid remains.

The result of further heating is merely for a time to raise the temperature; the acid does not distil in the anhydrous condition. At about 200° it begins to decompose slowly, and at higher temperatures rapidly, into selenium dioxide, oxygen, and water. The latter serves to dilute a portion of the remaining acid, which then at once distils. In order to examine the effect of distilling the anhydrous acid destructively in a vacuum, a portion was heated in a flask connected with a condensing arrangement until rapid decomposition took place. The residue always consisted of a mixture of anhydrous selenic acid with selenium dioxide, the proportion of the latter increasing with the rise of temperature and length of time of heating. The former was proved to be present by dropping in a crystal of anhydrous acid, when the liquid froze, and it also gave a colouration in the cold with the selenium test for the same acid, which will be described hereafter. A portion which had been distilled for some time left a residue of which 0·7107 grm. neutralised 18·50 c.c. of semi-normal soda solution, using litmus as indicator, equivalent to 94·27 per cent of acid calculated as selenic—a result which might be expected, owing to the influence of the selenium dioxide in diminishing the acidity, as has been already pointed out. The distillate consisted of selenium dioxide mixed with selenic acid. The latter was in a dilute state, since it would not solidify on addition of a crystal of anhydrous acid, nor would it respond to the selenium test: 0·4703 grm. neutralised 11·11 c.c. of seminormal soda solution, equivalent to 85·46 per cent of acid calculated as selenic. Taking into account the diminution of acidity caused by the selenium dioxide, it is evident that a very concentrated, although not anhydrous, acid distils over.

Action of Heat under Ordinary Pressures.—When dilute selenic acid is boiled at ordinary pressures nothing but water is evolved until 205° is reached, at which temperature it has the composition of the monohydrated acid. In these respects it behaves like dilute sulphuric acid. After passing 205° the distillate contains at first mere traces of selenic acid, but its strength gradually increases. A portion of acid distilled between 205° and 227° yielded a distillate of which 0·6826 grm. neutralised 0·10 c.c. of seminormal soda solution, equivalent to 0·53 per cent of selenic acid. On further heating from 227° to 260° a distillate was obtained, of which 0·3818 grm. neutralised 0·32 c.c. of seminormal soda solution, equivalent to 3·03 per cent of selenic acid. At the latter temperature the acid commenced to distil over in white fumes. 0·6878 grm. of the residue left at 260° neutralised 17·76 c.c. of seminormal soda solution, equivalent to 93·41 per cent of selenic acid. At higher temperatures a portion of the acid is decomposed, the distillate being kept weak by the water continuously set free in the decomposition; and at still higher temperatures much selenium dioxide also distils over. A portion of acid which commenced to boil at 235° was heated until the temperature rose to 325°: 2·1542 grms. of the distillate neutralised 3 c.c. of seminormal soda solution, equivalent to 5·04 per cent of selenic acid. The residue was then further heated until the geater part of the acid was decomposed, and the strength of the distillate taken: 1·6176 grm. neutralised 16·5 c.c. of seminormal soda solution, equivalent to 36·90 per cent of acid calculated as selenic, but much of the acidity was due to selenious acid, a large amount of which was present in the distillate. It is thus seen that the selenic acid which distils under ordinary pressures is always highly dilute.

When anhydrous selenic acid is strongly heated under ordinary pressures a portion of it is decomposed into selenium dioxide, oxygen, and water, the latter serving to dilute the remaining acid. It will then no longer solidify on addition of a crystal of the anhydrous acid. After further heating it becomes sufficiently dilute to distil over in the manner already described. It is instructive to compare with this the action which takes place in the case of anhydrous sulphuric acid. Marignac found (*Annales de Chimie et Physique* (1853), 39, 184) that the latter when heated gives off sulphuric anhydride until the remaining acid is reduced to the same strength as that yielded by a more dilute acid on prolonged ebullition—about 98·66 per cent. In the case of selenic acid the anhydride is evidently unable to exist free at elevated temperatures, but breaks up into selenium dioxide and oxygen.

It is worthy of note that a remarkable coincidence exists between the temperature at which selenic acid is decomposed, and that at which selenium dioxide sublimes. The latter is not stated very definitely in any of the chemical text-books; we have found, however, that at 280° rapid sublimation takes place, while at 250° volatilisation proceeds slowly. When selenic acid is kept for some time at the latter temperature it is always found to contain traces of selenium dioxide, while at 280° decomposition proceeds with rapidity. It is probable that a connection exists to a considerable extent between the phenomena, and that the explanation of the coincidence may be that the comparatively weak affinities which bind the molecule of selenic acid are unable to prevent its disruption when once a temperature is reached at which the tendency of its constituents to separate is aided by the expansion attending a change to the gaseous condition. We have seen that both phenomena are affected by the temperature; they are also dependent to some extent upon the pressure. Anhydrous selenic acid commences to dissociate in a vacuum at about 200°. We found that when selenious acid was heated under similar circumstances water was quickly evolved, and after prelonged heating of the residue a distinct white ring of selenium dioxide was deposited on the cold portion of the neck of the flask.

The Action of Sulphur upon Selenic Acid.

When powdered sulphur is mixed with liquid anhydrous selenic acid, there is no action in the cold; but if the mixture be heated to 63°, the sulphur dissolves in the acid with production of an exceedingly deep indigo-blue colour. There is some action, but slight, at 58°. The body which is produced is very unstable, since it begins to decompose at the temperature at which it is formed, with evolution of sulphur dioxide, and reduction of the selenic acid to selenious acid. If water be added when the colour has first developed, sulphur is deposited in soft yellow flakes; but after decomposition has commenced, the addition of water throws down red selenium chiefly, owing to the reaction between the sulphurous and selenious acids which are formed.

A similar action has long been known to occur between sulphur and sulphuric acid. In 1804 Buchholz (Gehlen's *Neues Journal der Chemie*, 3, 7) discovered that sulphur dissolved in the latter acid with the formation of a blue

* A Paper read before the Royal Society, May 2, 1889.

colour, the sulphur being re-precipitated on addition of water. This reaction was subsequently investigated by Vogel, Schweigger, Berzelius, Wach, and Stein, and in 1875 Weber succeeded in isolating the blue compound (Poggendorff's *Annalen der Physik und Chemie*, 156, 531), and discovered it to be a sesquioxide of sulphur, S_2O_3, but very unstable, decomposing at ordinary temperatures with evolution of sulphur dioxide.

The Action of Selenium upon Selenic Acid.

A reaction takes place between selenium and anhydrous selenic acid in the cold. The selenium dissolves in the acid with production of an intense and beautiful green colour. The presence of a minute quantity of water prevents the colour from developing fully until the acid is warmed. The acid is capable of dissolving a considerable quantity of selenium. If kept in a closed vessel the colour thus produced is very permanent, being unaffected for months during summer weather, but if the acid be heated to 75° the colour disappears, and the selenic acid is found to be partly reduced to selenious acid. Addition of water, when the colour has developed, throws down a voluminous red precipitate of selenium; and exposure to the air in an open vessel for a few minutes is sufficient, from the same cause, to change the green colour to red. It will be shown hereafter that this green colour is probably caused by the formation of a new oxide of selenium. Its production with the anhydrous acid affords a test for the latter, which we have already made use of in examining the effect of heat upon selenic acid.

In 1827 Magnus found that selenium was dissolved by strong sulphuric acid with development of a green colour, and was re-precipitated on addition of water. Berzelius and Fischer subsequently investigated the reaction, and in 1875 Weber (Poggendorff's *Annalen der Physik und Chemie*, 156, 545) isolated the green compound, and found it to be a sulphoxide of selenium, $SeSO_3$. The colour given by selenium with sulphuric acid is a dark green, not so bright as that which it produces with selenic acid.

The Action of Tellurium upon Selenic Acid.

Like selenium, tellurium reacts upon anhydrous selenic acid in the cold, but with production of a purple red colour. Even when the acid is not perfectly anhydrous, it will still give a colouration in the cold. The compound thus formed is probably very unstable, since the colour disappears at so low a temperature as 19°, the selenic acid being partly reduced to selenious acid. If water be added when the colour has developed, tellurium is thrown down in sooty flakes, and exposure to moist air produces the same effect.

Tellurium reacts in a similar manner with strong sulphuric acid with development of a red colour, and re-precipitation on addition of water. This was first observed by Müller von Reichenstein. In 1798 the same reaction was investigated by Klaproth, and afterwards by Magnus and Fischer. The red compound was isolated by Weber in 1882 (*Journal fur Praktische Chemie*, 25, 218), and soon afterwards independently by Divers and Shimosé (*Journal of the Chemical Society*, Transactions, 43, 319), and was ascertained to be tellurium sulphoxide, $TeSO_3$.

Comparison of Sulphoxides with Selenoxides.

The coloured compounds first formed by the action of sulphur, selenium, and tellurium upon sulphuric acid were subsequently produced by the action of the same bodies upon sulphuric anhydride, and were isolated by forming them in the latter manner, and then removing the excess of anhydride. As has been already mentioned, they were found to be sulphoxides having the composition respectively, SSO_3, $SeSO_3$, and $TeSO_3$. Considering the similarity of the reactions which produce them, and of the decompositions to which they are liable, it is very probable that the coloured bodies formed with selenic acid are selenoxides, analogous to the sulphoxides already known, the sulphur in the latter being replaced by selenium. A comparison of the formulæ of the two series of bodies as represented in the following table, leads to some interesting considerations:—

Colour of compound.	Sulphoxides.	Selenoxides.
Blue	SSO_3	$SSeO_3$
Green	$SeSO_3$	$SeSeO_3$
Red	$TeSO_3$	$TeSeO_3$

The green body formed by the action of selenium upon selenic acid is, in all probability, a new oxide of selenium, having the composition Se_2O_3, analogous to the sesquioxide of sulphur formed by the action of sulphur upon sulphuric acid.

The colour of the above compounds appears to be almost entirely due to the element which is added on to the anhydride; the sulphur or selenium in the residual portion of the molecule has scarcely any effect upon the colour.

The green body $SeSO_3$ must be metameric with the blue compound $SSeO_3$, and consequently the atoms of sulphur and selenium in each of these bodies must occupy dissimilar positions in the molecule.

The Possible Existence of Selenic Anhydride.

A consideration of the foregoing facts leads to the conclusion that selenic anhydride, which has not up to the present time been obtained, is yet capable of existing in a free condition. Just as the sulphoxides are direct addition compounds of sulphur, selenium, and tellurium respectively with sulphuric anhydride, so the selenoxides must be regarded as addition compounds of the elements mentioned, with selenic anhydride. It is difficult to conceive that bodies so constituted are capable of existing free, and that the anhydride is unable to do so. On the other hand, it is probable that it dissociates at a comparatively low temperature, but one that is higher than 75°—the highest temperature at which the most stable of the selenoxides has been as yet found to exist. Selenious anhydride is always obtained, and not selenic, under similar conditions to those which produce sulphuric anhydride, and involving a high temperature.

We have examined the action of heat upon various selenates. Those selected for the purpose were the selenates of antimony, bismuth, platinum, lead, and silver, and also ferric and mercuric selenates. In no instance was selenic anhydride obtained, but selenious anhydride was evolved in all cases when the above selenates were strongly heated.

Von Gerichten (*Liebig's Annalen der Chemie* for 1873, p. 214) endeavoured to form selenic anhydride in a similar manner to that by which sulphuric anhydride is usually obtained—by leading a mixture of oxygen and the vapour of selenious anhydride through red-hot platinum sponge. He states that in one experiment a white deposit was obtained which consisted partly of selenious anhydride, but probably also contained selenic anhydride, since it dissolved in water with a hissing sound, and the solution was found to contain selenic acid. In subsequent experiments a decidedly negative result was obtained, since only selenious anhydride was found in the product.

In order to examine if selenic anhydride is produced in the manner just described, the following experiments were made:—

Some platinum sponge was introduced into a combustion-tube, and a quantity of selenious anhydride placed behind it. The platinum sponge was kept at a red heat, and the selenious anhydride was also heated until it sublimed. Oxygen, which was first dried by passing through a series of tubes containing calcium chloride and sulphuric acid, was led through the platinum sponge, carrying the vapour of the selenious anhydride with it. A white deposit formed in front of the platinum sponge, which, on examination, was found to consist solely of selenious anhydride.

The last experiment was repeated, substituting selenium for selenious anhydride. The vapour of the

selenium, on passing through the platinum sponge, was oxidised to selenious anhydride, but no selenic anhydride was formed.

The next experiment was similar to the first, but platinum black was substituted for platinum sponge. As before only selenious anhydride was deposited.

In the next experiment selenious anhydride was mixed with platinum sponge, and placed within a tube arranged in such a way that it could be placed in an oil-bath. The temperature was then raised gradually to 250°, oxygen being led through continuously. At the temperature mentioned a sublimate formed, and this as well as the platinum sponge was treated with water and tested, but no selenic acid was found.

The next experiment was similar to the last, except that the selenious anhydride was mixed with platinum black instead of platinum sponge, but, as before, nothing but selenious anhydride was obtained.

As may be seen from the above experiments, we have been unable to confirm the observation made by Von Gerichten.

We have found that oxygen in the active condition is unable to oxidise selenious anhydride. Oxygen, which was first passed through a series of drying tubes, was ozonised by means of a Houzeau's ozoniser, and then led slowly through a tube containing selenious anhydride for three hours and a half. At the end of that time the tube was disconnected, the ozone displaced by a current of dried air, and the contents of the tube dissolved in water and tested for selenic acid, but no trace of it was detected.

The Selenates of Antimony, Bismuth, and Platinum.

In the examination of the action of heat upon selenates, the three above mentioned were included. We have been unable to find any published account of these, and accordingly give here a short description of them.

Antimonious Selenate.—This body was formed by heating metallic antimony with selenic acid until it dissolved, and then continuing the heating until the excess of acid was driven off. It forms a white crystalline mass, which under the microscope is seen to consist of minute prisms. It is not very soluble in acids, but on boiling with selenic acid for some time it dissolves slightly, but apparently without formation of an acid salt, as the crystals deposited on evaporating the solution have the same shape and size as the original salt. It is not decomposed on boiling with water, nor is it soluble; if, however, the excess of selenic acid has not been expelled in its preparation, a little of it dissolves in the weak acid formed, and crystallises out again on cooling.

Bismuthous Selenate.—This was prepared by boiling bismuthous carbonate with selenic acid, and continuing the heating until the excess of acid was expelled. It crystallises in minute white prisms. It is insoluble in water, and is not decomposed by it on boiling, but if selenic acid be present it dissolves. It is also soluble in sulphuric acid on boiling, and readily in hydrochloric and nitric acid. Potash and soda decompose it, uniting with the selenic acid.

Platinic Selenate.—This was prepared by heating platinic chloride with selenic acid until the hydrochloric and excess of selenic acid were expelled. It is a dark brown body, which dissolves slightly in water on boiling, forming a yellowish brown solution. It is insoluble in alcohol. It dissolves readily in hydrochloric acid, and leaves metallic platinum on ignition.

The Action of Phosphoric Anhydride upon Selenic Acid.

When sulphuric acid is heated strongly with phosphoric anhydride sulphuric anhydride is evolved; on the other hand, the effect of heating a mixture of anhydrous selenic acid and phosphoric anhydride to a high temperature is, that selenious anhydride is given off, and not selenic. In order to see if a different reaction occurs between the latter two bodies at a lower temperature, some anhydrous acid was mixed with phosphoric anhydride in a flask, which was then tightly closed and placed in the water-oven. After heating for some time a clear solution was obtained, and the flask was then removed and allowed to stand in the cold. Crystals were slowly deposited, which under the microscope were seen to be transparent cubes. The acid liquid was drained off, and the crystals examined. So far as an analysis could be carried out the results agree with the view that the body thus obtained is selenic anhydride, SeO_3, but the quantity of material at our disposal at the time was too small to admit of its satisfactory separation and examination. We are, however, at present engaged in operating upon larger quantities, and hope, at no distant date, to submit our results to the Royal Society.

Selenium Oxychloride.

It may be useful here to mention a reaction, hitherto undescribed, by which selenium oxychloride can be obtained. It consists in distilling a mixture of sodium chloride and selenium dioxide. The reaction is a simple one—

$$2SeO_2 + 2NaCl = Na_2SeO_3 + SeOCl_2.$$

Half the selenium remains as sodium selenite.

THE ACCURATE DETERMINATION OF CARBONIC ACID AND MOISTURE IN AIR.

By J. S. HALDANE, M.A., M.B.,
and M. S. PEMBREY, Pell Exhibitioner of Christ Church, Oxford.

(Continued from p. 258).

We at first directed our attention to the errors connected with weighing. The glass flasks hitherto used weighed from 110 to 115 grms., and on account of their weight had not been weighed on a very fine balance. The glass stoppers of the flasks had not been greased, and we suspected that the sulphuric acid had escaped at the sides of the stopper, and so given rise to errors. The flasks were also of an awkward shape for carrying about, and easily broken; and since it was essential to make the apparatus easily portable we decided to substitute for the flasks large test-tubes. Accordingly test-tubes (6 inches × 1 inch) were filled with soda-lime and pumice saturated with sulphuric acid, and provided with double bored corks. Through each cork there passed a longer glass tube reaching to the bottom of the test-tube, and a shorter one only passing downwards as far as the cork. The cork was covered with paraffin inside and out. Before use the tubes were carefully washed, and dried with a clean cloth. Each tube weighed about 70 grms. The weighings were done on a long-arm Oertling balance weighing with certainty to less than 0·0001 grm. The balance previously used was apt to give slightly different indications each time the knife edge was brought down. The precaution was also taken of leaving the tubes in the balance-room for at least half an hour before weighing, and placing them on the balance with as little handling as possible, so as to prevent the temperature being altered by the warmth of the hand. Even with the old balance better results were obtained on taking these precautions than previously. Thus in three experiments the second sulphuric acid tube varied −0·0005, −0·0004, and +0·0006. In two experiments on the absorption of CO_2 the test absorption-tubes in one case weighed exactly the same after the experiment as before, and in another case they lost 0·0020. In the following experiment all the weighings were made very carefully on the fine balance. 32 litres of air were aspirated through the tubes in thirty-three minutes.

* Read before the Royal Society, May 2, 1889. (From the Physiological Laboratory, Oxford).

Tube 1	+0·1986	
,, 2	+0·0001	
,, 3	−0·0049	together = +0·0207.
,, 4	+0·0256	
,, 5	−0·0197	together = +0·0006.
,, 6	+0·0203	

Since even the new test absorption-tubes sometimes gained and sometimes lost in weight, we determined to study the causes of these variations. It was of course a matter of the utmost importance for the method to eliminate as far as possible "errors of weighing," as otherwise it would be necessary in making analyses to aspirate inconveniently large quantities of air.

We at first thought that the errors of weighing might be due chiefly to alterations in the pressure and temperature of the air occurring between the weighings. A simple calculation shows that the difference from this cause in the weight of the air displaced by the apparatus must be very distinctly appreciable with a balance weighing to decimilligrms. We therefore weighed absorption-tubes at intervals, noting at the same time the variations in the height of the barometer and in the temperature of the room. The variations in weight did not, however, at all correspond with the variations in barometric pressure and temperature. These variations in weight occurred so rapidly at times that almost every swing of the balance showed a slight alteration in weight, and this alteration went on hour after hour, the change being sometimes in the direction of gain and sometimes in the direction of loss of weight. Occasionally there was no sensible change for two or three hours. The alteration occurred whether the tubes were stoppered or not, and amounted frequently to about 10 decimilligrms. in the course of several hours. Similar alterations were found to occur in a dry empty tube.

Probably the alterations were partly due to the varying state of saturation of the air with moisture, and consequent variations in the amount of moisture condensed on the outside of the glass tubes, and partly to diffusion of moisture into the tubes. We did not, however, pursue the inquiry further, since we found that the "error of weighing" could be entirely eliminated by the plan of weighing against a counterpoise consisting of a tube made exactly like a sulphuric acid or a soda-lime absorption-tube, and of about the same weight. This counterpoise is always kept in the same place as the absorption-tubes. It is left stoppered when they are stoppered,* and unstoppered when they are unstoppered. As during an experiment the absorption-tubes may have been cooled or warmed more than the counterpoise by the air passing through them, the weighing must be deferred for half an hour, so as to allow their temperatures to become equal again. The tubes are weighed unstoppered. Before weighing, the stoppers are removed from the whole of the tubes, including the counterpoise, and not replaced until the last tube has been weighed. No absorbent is kept inside the balance case. With these precautions we found that the tubes do not vary in apparent weight within twenty-four hours by more than 3 decimilligrms. at the most, and usually agree to a decimilligrm. Our weights, although apparently in good preservation, showed disagreements with one another which amounted with different combinations of weights to 2 decimilligrms., so that slight apparent remaining variations in weight of the tubes might be set down as mostly due to imperfections in the weights.

After the error of weighing had thus been disposed of, we proceeded to make new test experiments.

Experiment No. 1.

The tubes were arranged in series in the following order:—1, sulphuric acid; 2, sulphuric acid; 3, soda-ime; 4, sulphuric acid; 5, soda-lime; 6, sulphuric acid. 90 litres were aspirated through in ninety minutes. The aspirator in this and the following experiments was a Bunsen water-pump, and the air was measured by a gas-meter.

Tube 1	+0·5142	
,, 2	±0·0000	
,, 3	+0·0463	together +0·0868.
,, 4	+0·0405	
,, 5	−0·0221	together −0·0001.
,, 6	+0·0220	

Experiment No. 2.

Repetition of No. 1, 90 litres aspirated in ninety-one minutes.

Tube 1	+0·4712	
,, 2	+0·0002	
,, 3	+0·0372	together = +0·0721.
,, 4	+0·0349	
,, 5	−0·0164	together = −0·0007.
,, 6	+0·0157	

At the end of this experiment some particles of soda-lime were found in the tubing connecting tubes 5 and 6. Evidently a little soda-lime had been blown over during the experiment, and what had been left in the rubber tubing was doubtless the cause of the loss in weight of 5 and 6 together. To prevent a repetition of this loss some cotton-wool was placed in the soda-lime tubes between the soda-lime and the cork.

Experiment No. 3.

Repetition of No. 1, 90 litres aspirated in ninety-seven minutes.

Tube 1	+0·5742	
,, 2	+0·0011	
,, 3	+0·0360	+0·1198
,, 4	+0·0838	
,, 5	−0·0828	+0·0004
,, 6	+0·0832	

In this experiment there was an escape of moisture from tube No. 1; this tube had been used for a number of experiments in addition to those recorded above. It was not used again except as a counterpoise.

The experiment described seemed to show that a certain proportion of CO_2 escapes absorption by soda-lime, and is absorbed by baryta solution. Although we felt sure this was not the case, we, nevertheless, chiefly for the sake of testing the tube method of Pettenkofer, repeated the experiment with the following precautions:—

In addition to the six Pettenkofer tubes through which the air was passed, six others were taken, washed, and charged with the same quantity of baryta solution in exactly the same way as the first set. These dummy tubes were kept stoppered during the experiment. All the tubes were washed before the experiment, first with dilute nitric acid (1 to 10), then three times with tap water, and, finally, with distilled water; they were then dried in the usual way. 60 litres of air were aspirated in an hour. At the end of the experiment the baryta from each set of Pettenkofer tubes was poured into a ½-litre flask, and at once corked and allowed to stand for the night; during this process every precaution was taken to avoid unnecessary contact with the baryta-water.

Sulphuric acid, pair 1*	+0·4183
Soda-lime, pair 1. ..	+0·0554

Baryta from first set of Pettenkofer tubes .. (1) 40 c.c. = 39·9 c.c. standard oxalic.
(2) ,, = 39·9 ,, ,,

Loss of water by same tubes by evaporation 0·8408 grm.

* The stoppers used are the ordinary ones, consisting of a short piece of black rubber closed at one end by a piece of glass rod.

* The tubes were arranged in pairs, as described below.

Baryta from dummy set of Pettenkofer tubes	(1) 40 c.c.	= 39·65
	(2) „	= 39·75
	Mean	39·7

Standard baryta-water, 40 c.c. = 40·25.
Loss of alkalinity in first set = 6×0·35=2·1 c.c. standard oxalic.
Loss by evaporation .. .. =0·84
2·94 c.c.

Loss of alkalinity in dummy set = 6×0·55 = 3·30 c.c. oxalic solution.

The dummy tubes had thus actually lost slightly more in alkalinity than the tubes through which the air was passed. This result explains the loss in alkalinity in the baryta-water in the previous experiments.

The loss in the dummy tubes is equal to what would be caused by the absorption of 0·0033 grm. of CO_2, or the CO_2 contained in about 4 litres of air. Considering the scrupulous precautions which were taken, such a loss could hardly be due to the baryta-water coming in contact with air during the manipulations necessary. We thought that possibly the loss might be mostly due to the action of the glass on the baryta-water; and our experience called to mind a statement of Pflüger* that he found in making the titrations for Kjeldahl nitrogen determinations that it was impossible to titrate accurately in flasks which had been previously washed with acid. The glass seemed to retain part of the acid, and give it up again slowly during the analysis. We made several experiments as regard the bearing of this point on the Pettenkofer method, but the results were conflicting.

The above experiments proved that the absorption both of moisture and CO_2 was practically complete by the respective absorption-tubes, although the Experiment No. 3 seemed to show the escape of a scarcely weightable trace of CO_2. The absence of variation in weight of tube 2 in the first two experiments, and in others noted below, proves the groundlessness of the supposition of Hlasiwetz and others that CO_2 or any other gas present in air is absorbed by the sulphuric acid. Such an absorption is *primâ facie* highly improbable. The coefficient of absorption of sulphuric acid for CO_2 is, according to Setschenow, about equal to that of water, and a simple calculation shows that the variations in the amount of CO_2 occurring in any air ordinarily met with are too small to produce a weighable effect upon the amount held in absorption by the sulphuric acid. The case is of course quite different when large quantities of CO_2 are present, as in the gases from a combustion.

These experiments also show that there is no appreciable escape of CO_2 or moisture from outside through the junctions of the tubing into the air current. Pettenkofer believed that there is such an escape when the pressure in the tubing is negative, and therefore he drove the air through the absorption-tubes of his respiration apparatus instead of aspirating. Possibly, however, the escape observed by him may have been through the walls of the long pieces of rubber tubing connecting his absorption apparatus.

In order to save time and trouble in weighing, we now resolved to weigh tubes 1 and 2 and 3 and 4 together. The tubes were therefore made permanently connected in pairs. The final form given to them was shown by a drawing. The following are the details :—The test-tubes are 4×1 inch, and made of thin glass. Each tube is provided with a double-bored cork about ½ inch thick, which is fitted with glass tubing of about $\frac{1}{16}$ inch internal diameter, and in the form shown in the drawing.† The tubing must fit tightly; and the corks must be covered with a layer of paraffin inside and out. They are pushed down a very little below the top of the tube, the end of the tube being first warmed to soften the paraffin, and so facilitate the entrance of the cork. To prevent pieces of pumice or soda-lime getting into the tube during this operation a passage should first be cleared in the pumice or soda-lime with a piece of glass rod. Should, however, any soda-lime get into the tube and produce an obstruction, this can be easily pushed down from the outside by a piece of wire. As the figure showed, a plug of cotton-wool is placed between the surface of the soda-lime and the cork. A layer of paraffin is spread smoothly over the top of the cork until it is just level with the edges of the tube. In this way the risk is avoided of pieces of paraffin being knocked off during the weighings. The apparatus must be tested for tightness by means of an aspirating bottle or other simple arrangement, and should allow air to pass perfectly freely when suction is applied.

The pumice is sifted through a wire sieve with meshes ½-inch apart, and shaken in a fine one to remove the powder. It is then heated to redness by playing on it with a large blowpipe flame, and thrown still hot into sulphuric acid ("pure re-distilled.") The superfluous acid is then poured off, and the pumice preserved for use in a stoppered bottle. Before using the tubes for experiments we have always taken the precaution of washing them out with air. The air passed through them at first usually tastes slightly of sulphurous acid.

The soda-lime we have hitherto used was made by heating together in a copper vessel 2 litres of 60 per cent caustic soda solution, and the product obtained by shaking to a fine powder 1000 grms. of quick-lime. The heating was continued until the soda-lime became capable of being broken up into fragments in a mortar. The fragments were rapidly sifted in a wire sieve with meshes $\frac{1}{10}$ inch apart, and the product freed from powder by sifting in a finer sieve. We have also tried commercial soda-lime similarly sifted, and found that it absorbed CO_2 nearly as well.

Each pair of tubes weighs, when filled, about 80 grms.

The aspirator used was arranged as follows :—Two bottles, each holding about 3200 c.c. up to a mark on the neck, were provided with corks, the one with two holes bored in it, the other with three. Through each cork passed a long piece of tubing about ½-inch in internal diameter, and a short bent tube of a somewhat less diameter, the long pieces in the two bottles being connected together by a piece of stout, non-collapsing rubber tubing provided with a screw-clip and a burette-clip. The screw-clip is for regulating the flow of water once for all to about a litre per minute. The burette-clip is for stopping the flow during an experiment. The temperature of the water is measured by means of a thermometer inserted in a third hole in one of the corks. To prevent breakage, this thermometer should not project beyond the cork. The bottles are covered outside with a layer of felt, to keep the temperature of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched during an experiment. It is convenient to graduate the bottles roughly by passing strips of paper at intervals of half a litre up the uncovered strip of glass. With the help of this graduation it is easy to ascertain that the aspirator is running at about the proper rate.

To graduate the aspirator, one of the bottles is allowed to drain for a minute, and is then weighed. The two bottles are then connected and filled, so that both of the bottles are full to the mark, and the tubing is also full of water. The cork of the weighed bottle is removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again, and by deducting this weight from that of the empty bottle, and allowing for air displaced, &c., as in the graduation of a measuring flask, the

* Pflüger's *Archiv.*, vol. xxxvi., p. 105.

† The longer piece of glass tubing in the first sulphuric acid absorption-tube is made somewhat shorter than the corresponding tubing in the other absorption-tubes. The inconvenience arising from the collection of water in the first tube is thus avoided.

amount of water held by the bottle filled to the mark with the tubing in it is obtained. The difference between this amount, and some round number of c.c., such as 3000, is then measured into the bottle, which has been previously emptied and drained for a minute. The cork is then replaced, care being taken, as before, not to spill any of the water in the tubing. The aspirator is now ready for use.

The short piece of glass tubing of the bottle which is filled to the mark, is attached by rubber tubing to the absorption apparatus. The other bottle is then placed 2 or 3 feet below, and the burette-clip opened. It is always desirable to test the tightness of the whole apparatus before each experiment by opening the clip while the stopper is on the inlet tube of the absorption apparatus. The water is allowed to flow until the lower bottle is full exactly to the mark on the neck. The bottles are then reversed, if necessary, and the process repeated as often as required. In very foul air, such as that of ordinary schools without mechanical ventilation, one bottleful of air will be sufficient, as a rule. In free air, several bottlesful will be required, the number varying according to the accuracy aimed at.*

The thermometer must be read during the aspiration. It is doubtless well to have the temperature of the water as near as practicable to that of the air to be examined, but we found that with the felt jacket, a thermometer suspended in the air above the water, kept within 0·25 of a degree of the temperature of the water during the emptying of the aspirator, and for some minutes longer. This was on a windy day, and with the temperature of the water 6° C. above that of the air. The temperature of the water itself varies very slowly, but must be observed at intervals and the mean taken in a long experiment.

(To be continued).

NOTE ON THE

METHOD OF DETERMINING THE ATOMIC WEIGHT OF OXYGEN ADOPTED BY MR. W. A. NOYES.

By G. STILLINGFLEET JOHNSON.

In this paper, reprinted from the *American Chemical Journal* (vol. ii., No. 3) in the CHEMICAL NEWS (vol. lix., p. 224), a method is described for determining the atomic weight of oxygen by weighing the water formed on reducing copper oxide in hydrogen in the same vessel in which the reduction has taken place.

One source of error in the determination is indicated as possibly operating in his experiments by the author himself, viz., the retention by the copper (which has escaped complete re-oxidation) of hydrogen, occluded by the metal during its reduction in hydrogen gas. Other sources of error are clearly indicated in a paper of mine "On the Occlusion of Hydrogen by Copper," which was published in the *Journal of the Chemical Society*, May, 1879. As Mr. Noyes is evidently ignorant of the work done by Englishmen in this direction, and as the results obtained by me may prove interesting to some of the readers of the CHEMICAL NEWS, I have epitomised my work so far as it relates to the paper under discussion.

Four sources of error are perceptible to me in Mr. Noyes's method of experimentation, two of which are proved in my paper quoted above to be certainly operative, whilst the remaining two would come into play in case the copper employed contained sulphur.

1. The first certainly operative source of error is the one indicated by Mr. Noyes himself, *i.e.*, the retention of occluded hydrogen by incompletely re-oxidised copper. Mr. Noyes found it impossible to re-oxidise his copper completely, and he records two results which indicate a gradual oxidation of occluded hydrogen.

There are numerous experiments in the paper to which I have referred, in which it is clearly proved that copper will retain occluded hydrogen when heated to redness in a vacuum, but yields up its occluded hydrogen as water by combustion in carefully dried air.

2. The second source of error which in my opinion would certainly vitiate the accuracy of Mr. Noyes's results appears to have escaped his notice altogether. When copper oxide is reduced in hydrogen gas at temperatures below 700° C. I have found and recorded (*loc. cit*) that not only hydrogen, but actual water, is occluded by the reduced copper, and as this water was not carried away by a stream of hydrogen at the temperature of reduction, it would in all probability escape removal *in vacuo* at the same temperature. This retained water was, in my experiments, collected and weighed after its expulsion from the copper by ignition in pure nitrogen. Now, I find no record in Mr. Noyes's paper of the *temperature* at which his copper oxide was reduced, but I should gather from his description of the apparatus employed that it could not have exceeded 700° C., otherwise his glass bulb would have been in jeopardy.

As regards the third and fourth sources of error, they would operate only in case the copper employed contained sulphur. I am induced, however, to mention them, because the only guarantee given by Mr. Noyes of the purity of his copper oxide is that it was "Kahlbaum's best in wire form." Now, as I have never seen a specimen of commercial copper, even that obtained by electrolytic methods, which gave a negative result when tested for sulphur by solution in nitric acid and treatment with solution of baric nitrate, though in some cases the mixture must stand for some hours before the $BaSO_4$ comes down, I always conclude that sulphur is present until its absence has been proved by direct testing.

When sulphur is present in the copper, not only is the S not expelled completely during oxidation, but it is also retained in the metal after reduction in hydrogen, and, when the reduced copper is subsequently re-oxidised, H_2SO_4 is formed. All this is described in my paper (*loc. cit.*), and further, I proceed to describe the preparation of a sample of copper oxide free from sulphur, and to show that the metal obtained by reduction of this oxide in hydrogen occluded none of that gas, so that I would recommend the use of such copper oxide to future experimenters in this field.

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ON THE

DETERMINATION OF THE ORGANIC NITROGEN IN NATURAL WATERS BY THE KJELDAHL METHOD.*

By THOMAS M. DROWN, M.D., and HENRY MARTIN, S.B.

THE justification for the almost universal practice of determining the organic nitrogen in waters in the form of albumenoid ammonia is to be found in the great simplicity of the Wanklyn process. The amount of nitrogen obtained in the form of ammonia by the action of alkaline permanganate on nitrogenous organic matter in water bears no known relation to the total nitrogen present, and chemists report widely differing results in consequence of differing practice. In the case of colourless waters, with small amount of organic matter, the differences are not usually great, but in most surface

* About 30 c.c. of air are contained in the sulphuric acid absorption-tubes, and in some experiments it may be necessary to make an allowance for this air in calculating the results for CO_2. Such air contains, on an average, about 19 vols. of CO. per 10,000 of air.

* From the *Technology Quarterly*, Boston, vol. ii., No. 3.

waters, with considerable organic matter in suspension and solution, the results often differ fifty or one hundred per cent. Some water analysts stop the distillation for albumenoid ammonia when 150 c.c. have distilled over; others continue until 250 c.c. are obtained, and others, again, strive to get all the ammonia they can by the addition of more alkaline permanganate, or by replacing the water which has distilled over.

There can be no doubt that the determination of the total organic nitrogen would be generally practised in place of the determination of the albumenoid ammonia, if there was available a short, easily executed, and accurate method for this purpose.

As the result of a very large number of experiments with the Kjeldahl nitrogen process, we think it may be safely said that this method leaves little, if anything, to be desired in these respects.

The modifications of the process, as usually practised, to adapt it to the determination of organic nitrogen in waters, are in the direction of its simplification. Thus the amount of organic matter in water is ordinarily so very small that the use of solid potassium permanganate for the final and complete oxidation of the organic matter is probably never necessary. In most of the analyses which we have made, we have continued to use it as a matter of precaution, but in the comparative experiments, with and without its use, the results have not differed. The volumetric determination of the ammonia by titration with very dilute standard acid was found to be less accurate and less convenient than the Nesslerisation of the distillate, in the usual method employed in water analysis. Further, the same flask is used for both the digestion and the distillation.

Professor W. R. Nichols experimented with the Kjeldahl process for the determination of the nitrogen in sewage with satisfactory results,* but the process has not yet, as far as we know, been used in regular water analysis.

The examination is conducted as follows:—500 c.c. of the water is poured into a round-bottom flask, of about 900 c.c. capacity, and boiled until 200 c.c. have been distilled off. The "free ammonia" which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask is added, after cooling, 10 c.c. of pure concentrated sulphuric acid.† After shaking, the flask is placed in an inclined position on wire gauze, on a ring-stand, or other convenient support, and boiled cautiously, in a good-drawing hood, until all the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a very little powdered potassium permanganate added until, on shaking, the liquid acquires a green colour, showing that an excess of the permanganate has been added. Should the colour be purple instead of green, it shows that the water has not all been driven off. After cooling, 200 c.c. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 c.c. of sodium hydrate‡ solution. The flask is immediately connected with the condenser, and then shaken to mix the contents.

The distillation at the start is conducted rather slowly, and the first 50 c.c. are condensed in very dilute hydrochloric acid.§ The contents of the flask may then be boiled more rapidly until 150 c.c. to 175 c.c. have altogether been collected. The total distillate is made up to 250 c.c. with water free from ammonia, well mixed, and 50 c.c. taken for Nesslerisation. No serious difficulty has been encountered from bumping when boiling the alkaline solution. The use of metallic zinc in the flask to facilitate the boiling is, of course, inadmissible, on account of the reduction of nitrates and nitrites, should they be present, to ammonia.

Any efficient condensing arrangement may be used for the collection of the ammonia. We have used with great satisfaction the condenser devised by Prof. S. W. Johnson, of the Connecticut Agricultural Experiment Station, which is described in *Bulletin* No. 12 of the United States Department of Agriculture, Division of Chemistry. It consists of a copper tank, 20 inches high, 32 inches long, 3 inches across the bottom, widening to 6 inches at the top. The tank is provided with an adequate supply of running water, entering at the bottom, and accommodates 6 or 7 block-tin condensing-tubes, three-eighths inch internal diameter, which enter the tank through holes in the front side near the top, above the level of the overflow, and pass down vertically through the tank and out through rubber stoppers tightly fitted into holes in the bottom. They project about 2 inches below the tank, and are connected by means of rubber tubes to straight glass calcium chloride tubes with a bulb at the upper end. These glass tubes dip into 250 c.c. flasks which receive the distillate. The distilling-flasks are connected with the tin condensing-tubes by means of rubber stoppers which carry a bulbed glass tube bent at right angles. This tube and its rubber stopper remain permanently connected with the tin tube.

The flasks rest on iron rings, and are heated with the free flame of a Bunsen burner. They should be carefully selected as to size and height. And the fixtures should be so arranged that all parts are interchangeable. There is then never any difficulty in putting the flasks promptly into place and connecting them with the condenser.

It is a good plan to have flasks, partly filled with water free from ammonia, connected with the condensing-tubes when not in use.

Before beginning a determination the water in the flask is boiled until the distillate shows, on Nesslerisation, that the apparatus is completely free from ammonia. Into the flask which receives the distillate there is put 1 c.c. of the dilute hydrochloric acid and 50 c.c. of water. The delivery tube dips into this liquid only during the collection of the first 50 c.c. of the distillate. The flask is then lowered so that the tube remains above the liquid for the remaining time of the distillation.

In carrying out the operation, the most scrupulous care must be observed in preventing access of ammonia from any source. The acid solutions will absorb ammonia from the air of the laboratory or from the dust of the room if they are allowed to remain uncovered for any length of time. This source of error has been found at times to be very large; quite enough to render a determination valueless. One experiment gave a gain of ammonia in twenty hours, by leaving the flask which contained the concentrated sulphuric acid uncovered, equivalent to 0·5 c.c. of the standard ammonium chloride solution, and at another time the gain was 3 c.c.

The operation should therefore be carried out without interruption, and for every determination, or set of determinations, a blank analysis with ammonia-free water should be made for a correction for the ammonia in the reagents and that accidentally introduced in the process.

We have not found that the presence of nitrates and nitrites in waters interferes with the accurate determination of the organic nitrogen. The error which has been found by Kjeldahl and Warington* to be caused by nitrates in the determination of organic nitrogen seems to disappear under the conditions of great dilution which we have in natural waters.

* *Franklin Institute Journal*, August, 1885.

† It is necessary to have for this purpose sulphuric acid which is very nearly, if not quite, free from nitrogen in any form. Baker and Adamson, of Easton, Penn., make an acid for this purpose which contains only 0·005 m.grm. of ammonia in 10 c.c.

‡ The sodium hydrate solution is made by dissolving 200 grms. of commercial caustic soda of good quality in 1·25 litres of distilled water, adding 2 grms. of potassium permanganate, and boiling down to somewhat less than a litre. When cold, the solution is made up to a litre. The addition of the permanganate is to oxidise any organic matter which may be present in the caustic soda.

§ This acid should be free from ammonia; 1 c.c. of the acid is equivalent to 0·5 m.grm. of ammonia.

* Chemical News, liii., p. 162.

The following experiments bear on this point:—

1500 c.c. standard ammonium chloride solution (= 15 m.grms. NH_3) and 10 c.c. of standard potassium nitrite solution (= 1 m.grm. N) were boiled with 10 c.c. of sulphuric acid, and the vapours condensed. This distillate contained only 0·15 m.grm. nitrogen as ammonia and nitrous acid. The residue in the flask was made alkaline and distilled, and the ammonia obtained was precisely the amount taken, namely, 1500 c.c. The experiment was repeated, using a nitrate in place of the nitrite, and under the same conditions the 1500 c.c. of ammonia were recovered.

When a smaller amount of ammonia was used, we still failed to observe any loss. Thus when 10 c.c. standard ammoniun chloride solution and 10 c.c. potassium nitrite solution (= 0·1 m.grm. N) were treated as above, there was obtained ammonia equivalent to 10·5 c.c. Another experiment with the same quantities gave precisely 10 c.c. of ammonia regained. With potassium nitrate instead of nitrite, in the same proportions as in the foregoing experiment, 10·5 c.c. of ammonia were obtained.

The attempt to collect all the nitrous and nitric acids in the distillate was unsuccessful. The flask and condenser were connected by ground joints, so that the distillation could be continued after the sulphuric was concentrated. Owing, probably, to the shape of the flask, the acids were condensed, in part, in the neck of the flask, for after a second and a third addition of water and a renewal of the distillation more nitrous and nitric acids were obtained in the distillate. To see whether there was any loss of ammonia from ammonium sulphate in presence of sulphurous acid from the action of sulphuric acid on carbonaceous matter, the following experiments were tried:—10 c.c. of standard ammonium chloride solution were treated with 10 c.c. of sulphuric acid and a weighed amount of Swedish filter-paper. Deducting for the nitrogen in the paper, determined in a blank analysis, 10·5 c.c. of ammonia were obtained. In a duplicate experiment the ammonia obtained was 10 c.c.—precisely the amount taken. In still another experiment with 50 c.c. of standard ammonium chloride solution and filter-paper, 51 c.c. were obtained.

No attempt has been made to compare, as regard the results obtained, the above-described method of determining the organic nitrogen with the combustion method of Frankland and Armstrong. But the following experiments on very dilute solutions of organic substances of known composition may serve to confirm the accuracy of the method.

One hundred m.grms. of pure crystals of urea were dissolved in one litre of water free from ammonia. Ten c.c. of this solution were added to 500 c.c. of water, and the analysis conducted as above described. There was obtained 0·494 m.grm. of nitrogen, the theoretical amount being 0·466. In a duplicate experiment no solid potassium permanganate was added to complete the oxidation, and the result was 0·486 m.grm.

A solution of uric acid in dilute potassium hydrate was made of the same strength as the urea, and 10 c.c. taken for analysis. There was found 0·326 m.grm. of nitrogen; required, 0·333 m.grm. In a duplicate experiment without the permanganate, precisely the same amount was obtained.

A solution of naphthylamine, 100 m.grms. to the litre, was dissolved by the aid of dilute hydrochloric acid. An analysis of 10 c.c. gave 0·082 m.grm. nitrogen; required, 0·097. Here again the result obtained by the omission of the permanganate agreed precisely with the determination in which the permanganate was used.

The following series of experiments, made on a sample of Cochituate water, shows the very close agreement of results in the determination of organic nitrogen under varying conditions. From a large bottle of water freshly drawn from the tap were taken five portions of 500 c.c. each.

Comparison of Albumenoid Ammonia and Organic Nitrogen in Natural Waters.

I. *Surface Waters.*

Water.	Colour.	Albumenoid ammonia.	Organic nitrogen calculated as ammonia.
Arlington, Reservoir—			
June	0·8	0·0256	0·0560
July	0·3	0·0274	0·0560
Boston Supply, Basin 4—			
June	1·0	0·0226	0·0470
July	0·7	0·0234	0·0400
August	0·9	0·0254	0·0460
Boston Supply, Basin 2—			
June	1·4	0·0350	0·0590
July	1·3	0·0294	0·0450
August	0·85	0·0234	6·0440
Boston Supply, Basin 3—			
June	1·9	0·0392	0·0790
July	1·7	0·0336	0·0540
August	0·8	0·0278	0·0590
Boston Supply, Lake Cochituate—			
June	0·35	0·0176	0·0420
July	0·10	0·0192	0·0390
August	0·10	0·0196	0·0420
Boston Supply, Mystic Lake—			
June	0·20	0·0252	0·0590
July	0·10	0·0244	0·0560
August	0·15	0·0212	0·0420
Bridgewater, Taunton River—			
June	2·3	0·0248	0·0520
July	1·0	0·0210	0·0440
August	0·7	0·0212	0·0390
Brockton, Reservoir—			
June	0·9	0·0234	0·0570
July	0·9	0·0260	0·0490
August	0·7	0·0310	0·0610
Brookline, Charles River—			
June	1·20	0·0320	0·0520
July	0·60	0·0216	0·0470
August	0·45	0·0208	0·0380
Cambridge, Fresh Pond—			
June	0·20	0·0162	0·0370
July	0·15	0·0170	0·0390
August	0·0	0·0172	0·0390
Clinton, Nashua River—			
June	0·1	0·0072	0·0230
July	0·2	0·0144	0·0360
August	0·2	0·0124	0·0320
Fitchburg, Reservoir—			
June	0·1	0·0124	0·0250
July	0·1	0·0158	0·0340
August	0·1	0·0146	0·0240
Great Barrington, Housatonic River—			
June	0·1	0·0122	0·0320
July	0·1	0·0120	0·0270
August	0·0	0·0134	0·0320
Nashua, Merrimac River—			
June	0·4	0·0120	0·0320
July	0·2	0·0132	0·0290
August	0·2	0·0106	0·0290
Lowell, Merrimac River—			
June	0·30	0·0142	0·0420
July	0·10	0·0148	0·0280
August	0·25	0·0134	0·0320
Haverhill, Merrimac River—			
June	0·40	0·0164	0·0490
July	0·20	0·0170	0·0420
August	0·20	0·0163	0·0348

Water.	Colour.	Albumenoid ammonia.	Organic nitrogen calculated as ammonia.
Lake Winnepesaukee—			
June	0·0	0·0090	0·0230
July	0·0	0·0082	0·0190
August	0·0	0·0080	0·0200
Hyde Park, Neponset River—			
June	0·6	0·0286	0·0520
July	0·8	0·0432	0·1100
Lynn, Birch Pond—			
June	0·45	0·0194	0·0420
July	0·35	0·0216	0·0410
August	0·25	0·0174	0·0410
Malden, Spot Pond—			
June	0·3	0·0216	0·0440
July	0·2	0·0198	0·0390
August	0·2	0·0216	0·0390
Montague, Connecticut River—			
June	0·15	0·0120	0·0220
July	0·20	0·0118	0·0250
Springfield, Connecticut River—			
June	0·4	0·0132	0·0390
July	0·15	0·0146	0·0320
August	0·15	0·0170	0·0380
New Bedford, Acushnet River—			
June	2·3	0·0296	0·0540
July	1·8	0·0278	0·0540
Northboro, Assabet River—			
June	0·7	0·0192	0·0490
July	0·4	0·0216	0·0380
August	0·4	0·0174	0·0410
Salem, Wenham Lake—			
June	0·10	0·0132	0·0320
July	0·05	0·0118	0·0290
August	0·00	0·0130	0·0260
Springfield, Ludlow Reservoir—			
June	0·10	0·0222	0·0460
	0·20	0·0214	0·0440
July	0·10	0·0220	0·0420
August	0·05	0·0198	0·0390
	0·10	0·0206	0·0370
Wayland, Reservoir—			
June	1·5	0·0272	0·0590
July	0·9	0·0364	0·0660
August	0·4	0·0244	0·0540
Whitman, Hobart's Pond—			
June	1·7	0·0538	0·0990
July	1·5	0·0426	0·0990
August	0·9	0·0342	0·0740
Wilmington, Shawsheen River—			
June	0·8	0·0242	0·0640
July	0·15	0·0114	0·0370
August	1·00	0·0316	0·0570
Woburn, Horn Pond—			
June	0·35	0·0290	0·0570
July	0·25	0·0324	0·0590
August	0·10	0·0240	0·0440
Worcester, Blackstone River—			
June	—	0·0350	0·1350
July	—	0·0440	0·1550
August	—	0·0830	0·3800

II. *Ground Water.*

(Without Colour).

Water.	Albumenoid ammonia.	Organic nitrogen as ammonia.
Brookline, Filter Gallery—		
June	0·0046	0·0190
July	0·0046	0·0220
August	0·0042	0·0170
Newton, Filter Gallery—		
June	0·0044	0·0190
July	0·0072	0·0160
August	0·0052	0·0100
Revere, Wells—		
June	0·0018	0·0034
July	0·0034	0·0070
August	0·0018	0·0100
Revere, Reservoir—		
June	0·0034	0·0130
July	0·0046	0·0150
August	0·0060	0·0190
Waltham, Filter Gallery—		
June	0·0030	0·0170
July	0·0050	0·0160
August	0·0056	0·0150
Waltham, Reservoir—		
June	0·0042	0·0230
July	0·0042	0·0180
August	0·0060	0·0160

The first portion was treated by the usual method, already described.

The second portion was treated like the first, except that the addition of solid permanganate was omitted.

The third portion received 10 c.c. of standard potassium nitrate solution, equivalent to 0·1 m.grm. of nitrogen.

The fourth portion received 1 c.c. of potassium nitrite solution, equivalent to 0·01 m.grm. of nitrogen.

The fifth portion contained ten times the amount of potassium nitrite as the fourth portion, or 0·1 m.grm.

The third, fourth, and fifth portions were treated in all respects like the first portion.

The results, expressed in organic nitrogen, parts per 100,000, were—

No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
0·0354	0·0354	0·0354	0·0365	0·0365

It may be of interest to give a few of the results obtained in the determination of the organic nitrogen by this method in natural waters in comparison with the results obtained as albumenoid ammonia. In the Table will be found the analyses of some Massachusetts waters during three successive months, June, July, and August, 1888.

In the first column is a record of the colour, based on a comparison with the Nesslerisation of a known amount of ammonium chloride. Thus a colour 1 means that the water possessed a colour corresponding in depth and tint to 1 c.c. of standard ammonium chloride solution (=0·00001 grm. NH_3) when Nesslerised; a colour of 2 is twice the depth of colour, and 0·1 is one-tenth the colour of one. In the second column is the albumenoid ammonia obtained by the adding 40 c.c. of alkaline permanganate to the water in the flask, after boiling off 150 c.c. for free ammonia, and then distilling over 250 c.c. In the third column is the organic nitrogen determined by the Kjeldahl process, converted into ammonia to make the figures comparable with the second column. All the determinations were made on the waters filtered through paper in the laboratory.

It will be noted that the organic nitrogen in the surface waters is in general about double the albumenoid ammonia. The average of all the analyses of these waters given above is 0·0214 for the albumenoid ammonia, and 0·0476 for the organic nitrogen. In the ground waters the relation of the albumenoid ammonia to the organic nitrogen is still less. Too much importance must not, however, be given to this relation in the case of the ground waters, for it is probable that the figures given for the organic nitrogen are all a little high, owing to the fact that all of the sources of error were not fully known when most of the analyses were made. The proportional excess

in case of the surface waters is believed to be insignificant, but with the smaller content of nitrogen in the ground waters the error is perhaps proportionately large.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

May 25, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MR. T. A. LAWSON was elected a member.

The thanks of the Society were given to Mr. T. H. Blakesley for presenting to the library a copy of the second edition of his work on "Alternate Currents."

The following papers were read :—

"*On a Relation Existing between the Density and Refraction of Gaseous Elements and Some of their Compounds.*" By Rev. T. PELHAM DALE.

In a previous communication the author pointed out a relation between the specific refractive energies of sulphur and selenium, and the present paper deals with similar relations in gaseous bodies. On calculating out the values of—

$$\frac{\mu-1}{d}$$

for the elements H, O, N, Cl, S, P, it was noticed that the logarithms were nearly integral multiples of half the logarithm for H, those for N, Cl, and P being double and S and O three times that number. The value of $\mu-1$ for different elements is compared with the $\mu-1$ for H, the resulting numbers being for oxygen 2, mercury 7, arsenic 8, and sulphur 12 nearly. Similar calculations are made for the compounds N_2O, NO, CO, SO_2, Cy, NH_3, HCl, H_2S, CH_4, and C_2H_4, but as the data obtainable are very rough the numbers are not so closely integral. The author hopes that better data will be furnished by persons having greater facilities than himself for experimental research.

Prof. RÜCKER thought the results obtained pointed towards some relation between the volumes of the molecules of different elements, and, at the close of the meeting, announced that on working out the relation he found the relative volumes to be a series of numbers in geometrical progression.

"*On a Waterspray Influence Machine.*" By Mr. GEORGE FULLER.

The apparatus is made up of four similar sections, each consisting of a nozzle, a metal ring, and a metal dish or receiver, arranged about a vertical axis. Pressure water issues from perforations 1-100th inch in diameter in the nozzles, and passes through the ring into the insulated receiver below. The rings are placed at such a distance below the nozzles as to be about the point where the streams break into spray, and the receivers empty themselves automatically. Calling the consecutive sections 1, 2, 3, 4, respectively, the rings of 1 and 3 are connected to the receiver of 4, and those of 2 and 4 to the receiver of 1. The discharge points are connected with the receivers 2 and 3, and a rapid succession of sparks passes when the water is turned on.

Prof. S. P. THOMPSON enquired whether the length of the spark was limited by leakage along the glass rods, or by the spray passing between the receivers, and in reply

Mr. FULLER said he thought the former leakage the most important.

"*Notes on Polarised Light.* (*a*) *On the Transition Tints of Various Orders.* (*b*) *Lecture Illustrations of the Rotation of Circularly Polarised Light.* (*c*) *On the Rotation of Circularly Polarised and Non-polarised Light.*" By Prof. S. P. THOMPSON.

The first note described an enquiry as to what thickness of quartz gives the best "sensitive tint" for polarimetric work. Biot gave the name to the tint produced by a quartz 3¾ m.m. thick in a bright field, whereas, in most modern polarimeters, the name is given to that produced by 7½ m.m. quartz in a dark field. The transition tints of various orders were exhibited on a diagram of Newton's scale of colours and by a wedge of selenite. Experiments were made on quartzes of 3¾ and 11¼ m.m., giving tints of the first and second order respectively in the bright field, and with a 7½ m.m. quartz in a dark field. The 3¾ was more sensitive than the 11¼ to small rotations, but the 7½ m.m. seemed the best of the three. Prismatic analysis of the light transmitted by each led to the same conclusion, a new square-ended direct vision prism, built up of a glass prism (angle 140°) immersed in cinnamic ether, being used for that purpose. The author pointed out that the "sensitive tints" of German opticians are decidedly redder than Biot's and those generally used in England.

In the first apparatus described under (*b*) the ray of light is represented by a stretched cord thrown into promiscuous vibration by a tuning-fork, and the polariser and analyser are each represented by two plates of glass mounted parallel to each other about a millimetre apart, between which the cord passes. Between the polariser and analyser the vibrations are in one plane, and they are transmitted or cut off by the analyser according as its plates are parallel or perpendicular to those of the polariser. By blowing across one side of the spindle-shaped vibrating segment between the crossed plates the plane of vibration is slightly rotated and part is transmitted through the analyser. Other experiments illustrating rotation of the plane of polarisation were shown or described, the most conclusive being a bar of heavy glass placed along with a fish-eye lens between crossed Nicols. On starting a current in a helix surrounding the glass the black cross formed by the fish lens is seen to turn round as the current grows. Another piece of apparatus to illustrate Fresnel's view of the circularly polarised waves in quartz consists of two equal co-planar discs rotating in opposite directions, and carrying pins on which the extremities of a double pantograph arrangement are pivotted. The middle point of the linkwork describes a line perpendicular or inclined to the line of centres of the discs according as the phases of the pins are the same or different.

Note (*c*).—In speaking of rotary polarisation it is customary to say that the plane of polarisation is rotated, but the author thinks it is equally correct to say that the light itself is rotated. Prof. Stefan's and Prof. Abbé's experiments bearing on the subject were described, and to demonstrate that ordinary light may be rotated, a bi-quartz was placed between a Fresnel bi-prism and the screen on which the interference fringes were formed. By using quartzes of thickness sufficient to rotate each beam 45° the interference fringes are caused to disappear, and on inserting a bar of heavy glass in each of the pencils and magnetising one of them the fringes re-appear.

Mr. GLAZEBROOK thought the reason why 3¾ m.m. quartzes were more sensitive than 11¼ might be seen by considering the sector-shaped spectrum in which the rays are spread out by the quartz, for with the thick piece the angle of the sector will be three times that in the thin one, and hence, in the latter case, a greater change of colour is produced by a given small rotation.

Mr. WARD strongly condemned the use of bi-quartzes for rotation experiments, for he found it impossible to get them cut with such accuracy as to give a uniform tint, and if the light be slightly elliptically polarised considerable error may be introduced. Speaking of magnetic rotation, he thought Fresnel's explanation unsatisfactory, and considered it probable that the rotary character of the magnetic field increases the period of one and decreases that of the other circular wave, their velocities remaining the same. As regards quartz, he believes the

rotary action due to the light itself (probably an effect of the longitudinal wave) and not to any peculiar crystalline structure of the quartz, for liquids exhibit similar phenomena.

Dr. Thompson, in reply, said Mr. Glazebrook's explanation of the difference in sensibility of the quartzes of various thicknesses was not quite satisfactory, for the reasoning would lead one to expect the 3¾ m.m. to be most sensitive, whereas experiment showed that the 7½ m.m. was best. He quite agreed with Mr. Ward about the defects of the bi-quartz, and thought the shadow method preferable in many cases. On the other hand, he was disposed to believe that the rotary power of quartz was a result of its crystalline structure, for fused quartz possessed no such property. As regards liquids, Dr. Thompson thought the rotation due to some kind of skew symmetry possessed by the molecules, the average effect of which is observed.

"*On the Molecular Weight of Caoutchouc and other Colloid Bodies.*" By Dr. J. H. Gladstone, F.R.S., and Mr. W. Hibbert, F.I.C.

This paper gives the results of determinations made by Raoult's method, the reliability of which was first tested by preliminary experiments on substances of known molecular weights, and found to be fairly satisfactory. The experiments on caoutchouc give a very high value (above 6000), thus confirming the authors' previous impression that it was a colloid. Similar experiments were made on gum-arabic, caramel, albumen, and ferric and aluminic hydrates, all of which were found to have high molecular weights. All the experiments confirm the belief that the molecule of a colloidal substance is an aggregate of a very great number of atoms.

CORRESPONDENCE.

SEPARATION OF SILICA AND SAND.

To the Editor of the Chemical News.

Sir,—In an article on "Indigo Stem Ash" (Chemical News, vol. lix., p. 244) Mr. John Tsawoo White questions the possibility of perfectly separating silica from sand, after the mixture has been ignited, by means of sodium carbonate solution.

I can entirely confirm Mr. White's suspicions, for my own experience tells me that if silica has been ignited at a temperature sufficiently high to ensure the expulsion of the last traces of water (the use of the blowpipe, or, better, a muffle is necessary), it will by no means completely dissolve in sodium carbonate, even on long digestion. It is therefore needful to effect the separation while the silica is still in the hydrated condition.—I am, &c.,

Bertram Blount.

Laboratory, Broadway, Westminster, S.W., April 28, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 19, May 13, 1889.

Thionic Series. Action of Acids upon the Hyposulphites.—M. Berthelot.—The author studies thermochemically the displacement of hyposulphurous acid by boric acid, which in the cold is nil; by acetic acid, which has only a very minute effect; by sulphuric and hydrochloric acids.

On Mesocamphoric Acid.—C. Friedel.—Mesocamphoric acid is an isomer of camphoric acid obtained by heating dextro-camphoric acid to 140°—160° for thirty hours with an aqueous solution of hydriodic or hydrochloric acid. So far from being an inactive acid, it is split up by mere crystallisation into two acids, one dextro- and the other lævo-, of equal rotatory powers, but differing in their physical properties.

The Study of the Electro-conductivity of Saline Solutions applied to the Problems of Chemical Mechanics. Acid Salts.—P. Chroustchoff.—The author gives a table of the electro-conductivities of watery solutions, each containing merely a single salt.

Action of Air on Manganese Carbonate. Question if this Reaction can give Rise to any Manganese Dioxide.—A. Gorgen.—Experiment seems to show that at the common temperature manganese carbonate or oxide cannot absorb, in contact with air or aërated water, a proportion of oxygen greater than that present in the compound MnO_2MnO; hence we cannot assume that in nature manganese carbonate, deposited from its carbonic solutions, can give rise to deposits of manganese dioxide

On Platinic Chloride.—L. Pigeon.—The author has succeeded in obtaining platinum chloride by operating on a mixture of platinum and selenium in a stout glass tube partly filled with arsenic chloride, traversed by a rapid current of dry chlorine, and gradually heated to a boil in an oil-bath. The matter first obtained is a compound of platinum chloride and selenium chloride. On heating to 200° the latter sublimes, and platinic chloride remains. Platinum chloride is stable, at least up to 360°.

Certain Compounds of Nitric Oxide and of Hypoazotide with Anhydrous Chlorides.—Nitric oxide reacts with a great liberation of heat upon anhydrous antimony pentachloride, yielding a yellow crystalline body, $2SbCl_5NO_2$. Nitric oxide gives also direct combinations with anhydrous bismuth chloride and with anhydrous ferric and aluminic sesquichlorides. All these bodies are decomposable by water. Hypoazotide (NO_4) also forms analogous combinations under similar circumstances.

The Solubility of Salts. Reply to M. Le Chatelier.—H. W. Bakhuis Roozeboom.

The Solubility of Salts. New Reply to M. Roozeboom.—H. Le Chatelier.—A continuation of the controversy which we have already noticed.

Action of Borax upon the Polyatomic Alcohols.—Aug. Lambert.—The author concludes that the polyatomic alcohols possessing the primary function, and they only, can combine with boric acid to form energetic conjugated acids capable of decomposing carbonates, but becoming dissociated if diluted. The polyglucosides (saccharose, lactose, &c.) do not contain primary alcoholic groups, and have, consequently, a molecular constitution analogous to that of quercite and mannite.

Action of Borax on the Polyatomic Phenols.—Aug. Lambert.—If a small quantity of borax is added to a strong solution of pyrogallol, sodium monoborate is formed and a boro-conjugated acid capable of decomposing carbonates. Pyrogallol acts upon borax, as do glycerin and the mannites. Pyrocatechine, the gallates, and the tannates behave in a similar manner, but there is no action with orcine, resorcine, or hydroquinone.

On the Richness of Wheat in Gluten.—E. Gatellier and L. L'Hote.—The author thinks that it may be possible both to obtain a heavier crop and an increase in the proportion of gluten.

Biedermann's Central-Blatt fur Agricultur Chemie. Vol. xviii., Part 5.

On Paragalactine and γ-Galactan.—Prof. E. Schulze, Dr. E. Steiger, and Dr. E. von Lippmann.—

Paragalactin forms about 25 per cent of lupin-seeds extracted with water, alcohol, and ether. Like β-galactan, it is converted into galactose if it is heated with dilute sulphuric acid. γ-Galactan, $C_6H_{10}O_5$, obtained from the residues of beet-sugar, is strongly dextro-rotatory, and on boiling with dilute acids it yields galactose.

On the Glucoses obtained from Raffinose, and on Crystalline Saccharolactonic Acid.—Dr. Hädicke, J. Gans, Dr. Sohst, and Prof. B. Tollens.—From *Liebig's Annalen*.

Detection of Nitric Acid in Waters and Soils.—E. Bréal (*Annales Agronomiques*).—Nitrates dissolved in water accumulate by means of capillarity where evaporation is most rapid. The author therefore uses strips of white filter-paper, which must be previously freed from nitrates by careful washing—which he places with one end in the water to be examined whilst the other end is in the air. The nitrate gradually rises and accumulates at the extremity of the paper. Even if nitric acid is present in very minute traces in from twelve to fifteen hours they will all have collected in the extreme 1—2 m.m. of the paper. This is then cut off, put in a porcelain capsule, let dry, and then touched with a small drop of sulpho-phenol. If nitric acid is present the paper turns blood-red, and, on the addition of ammonia, becomes blue or green.

Action of the Alkaline and Earthy-Alkaline Metals upon the Animal Organisms.—A. Curci.

The Resistance of Pollen.—P. Rittinghaus (*Naturforscher*).—Most kinds of pollen can bear a temperature of 90° in dry air for fifteen minutes without losing its vitality. In moist air it is more easily destroyed. The plasma of pollen is generally more susceptible to antiseptics than are micro-organisms.

The Signification of the Colouring-matter of Chlorophyll.—A. Hansen.—The author considers that this pigment attracts carbonic acid, forms with it an unstable compound, and hands it over again to the assimilating plasma of the chlorophyll granules. It is, therefore a carrier of carbonic acid.

Action of the Alkaloids on the Animal and Vegetable Kingdoms.—A. Marcacci.—Seeds, roots, and plants all experience more or less the influence of certain alkaloids. From this point of view there is no sharp line of distinction to be drawn between animal and vegetable protoplasm. Still less can poisons be classified as acting upon animals or upon plants.

Ericaceæ on Calcareous Soils.—Prof. Julius Kühn.—The dictum that representatives of the ericaceous family never grow on calcareous soils is incorrect. *Rhododendron hirsutum* grows only on lime soils, whilst its near ally, *R. ferrugineum*, grows only on soils poor in lime. *Calluna vulgaris* (to which we may add *Erica tetralix*) and *E. cinerea*) avoid lime, whilst *E. carnea* grows in abundance on dolomitic soils.

MEETINGS FOR THE WEEK.

Tuesday, 11th.—Royal Institution, 3. "Some Recent Biological Discoveries," by E. Ray Lankester.
—— Royal Medical and Chirurgical, 8.30.
Wednesday, 12th.—Microscopical, 8.
Thursday, 13th.—Royal Institution, 3. "Chemical Affinity," by Professor Dewar.
—— Mathematical, 8.
Friday, 14th.—Royal Institution, 9. "Quartz Fibres," by C. V. Boys, F.R.S.
—— Astronomical, 8.
—— Quekett Club, 8.
Saturday, 15th.—Royal Institution, 3. "Idealism and Experience in Art and Life," by W. Knight, LL.D.

TO CORRESPONDENTS.

T. and R. W. Bower.—An electric spark would inflame coal-gas if passed across it in a space to which the air had access. If in a space entirely enclosed, and supposing the sparks to be frequent and of great intensity, the gas would be decomposed with deposition of carbon.

IMPORTANT WORK ON ECONOMIC BOTANY.

In Crown 8vo., Cloth Gilt, Price 6s., post free.

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A Manual of Economic Botany. With Special References to Vegetable Products Introduced during the last Fifty Years. By G. S. BOULGER, F.L.S., F.G.S., Professor of Botany at the City of London College, Author of "Familiar Trees," &c.

This work aims at giving a concise enumeration, with a systematic Index, of the Vegetable Substances in use in England as Food, Materia Medica, Oils, Gums, Rubbers, Dyeing, Tanning, and Paper-making Materials, Fibres, Timber, &c., both home-grown and imported, together with short essays on the recent progress of Vegetable Technology in its various branches.

CONTENTS.

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1.—Economic Botany more than Fifty Years ago.
2.—The Progress of Economic Botany in England during the last Fifty Years (1837-1887).
Part 1.—Foods, Food-stuffs, and Food-adjuncts.
Section 1. Starches and Bread-stuffs.
" 2. Sugars.
" 3. Pulse.
" 4. Roots and Tubers.
" 5. "Vegetables."
" 6. Fruits.
" 7. Nuts.
" 8. Food-adjuncts.
1. Alcoholic.
2. Condiments.
3. Flavourers.
4. Alkaloids.
Part 2.—Materia Medica.
" 3.—Oils and Oil-seeds, &c.
" 4.—Gums, Resins, &c.
Section 1. Gums.
" 2. Resins.
" 3. Caoutchoucs and Guttas.
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TO MANUFACTURING CHEMISTS and OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1575 tons of MANGANATE OF SODA, to be delivered at the rate of not less than 100, nor more than 200 tons per week, from the 1st July, 1889.

Persons tendering will be required to declare in their Tender that they pay such rates of wages, and observe such hours of labour, as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council at the office, Spring Gardens, until Monday, the 17th June, 1889. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed Tender for Manganate, and be sent in not later than 10 o'clock on Tuesday morning, the 18th inst.

The Council does not bind itself to accept the lowest or any Tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
6th June, 1889.

TO MANUFACTURING CHEMISTS and OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 1375 tons of SULPHURIC ACID, to be delivered as required, from the 1st July, next.

Persons tendering will be required to declare in their Tender that they pay such rates of wages, and observe such hours of labour, as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the office, Spring Gardens, until Monday, the 17th June, 1889. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed Tender for Sulphuric Acid, and be sent in not later than 10 o'clock on Tuesday morning, the 18th inst.

The Council does not bind itself to accept the lowest or any Tender.

H. DE LA HOOKE,
Clerk of the Council.

Spring Gardens, S.W.,
6th June, 1889.

THE CHEMICAL NEWS.

Vol. LIX. No. 1542.

NOTES OF RECENT AND FUTURE RESEARCH. THE SYNTHESIS OF URIC ACID.

By SAMUEL E. PHILLIPS, F.C.S.

In a paper read before the British Association, 1877, I recommended the simple and easy synthesis of uric acid, which had so long been a bone of contention with chemists, and further elucidation was referred to in the Chemical News, vol. xxxii., p. 209, and vol. xxxix., p. 28.

It was not a matter of numerical guess-work, but an estimate of reactions, supported by the widest and clearest evidence, and confirmed by every item of M. Grimaux's numerous ureide syntheses.

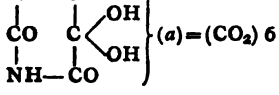
My contention was that uric acid would prove to be an ultimate of tartronic acid di-ureide. That as tartronyl anhydride + urea − 2HO gave tartronyl urea, miscalled dialuric acid on its empirical discovery; so tartronyl urea + urea − 4HO would give the elements of uric acid, thus:—

$$(CO)_2\ 6\ 1\ 6\ H_3N_2 + CO_2H_4N_2 = (CO)_4\ (C_6H_1O_6)\ H_7N_4\ (a)$$
$$-2HO = (CO)_2Cy\ (6\ 1\ 6)\ H_5N_3\ (b)$$
$$-2HO = Cy_2\ (6\ 1\ 6)\ H_3N_2\ (c)$$

(*a*) being the normal di-ureide, (*b*) pseudo-uric acid, and (*c*) the ultimate, uric acid.

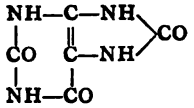
Nature of May 16th announces with much interest that M. Behrend has now synthesised uric acid, which proves to be *in the strictest accordance with the above.* But let us remark that in the meantime M. Horbaczeweski had actually produced this so-called acid, by a very complex high temperature reaction from glycocine and urea. But my impression of its extreme vagueness seemed confirmed by the latest opinions formed of that reaction, that it was a ureide derivative of acrylic acid. Then we find that "glycocine, leucine, aspartic acid, as well as urea itself, when brought into the organism of fowls, are changed into uric acid, as found in the urine." Added to all this we find that certain reactions with uric acid lead to the formation of tartronyl compounds; so much so that some eminent chemists have maintained that it must be a derivative of tartronic acid or of tartronyl urea.

We now compare this with the synthesis of M. Behrend. It is a very round-about process, but as tartronyl urea has long been known and identified we may well pass over, as quite superfluous, the first five stages; and, commencing with No. 6, we have malonyl urea (barbituric acid = $(CO)_2\ 6\ 1\ 4\ H_3N_2$) oxidised by bromine-water to tartronyl urea or dialuric acid, $(CO)_2\ 6\ 1\ 6\ H_3N_2$, which is notated:—



$$(a) = (CO_2)\ 6\ 1\ 6\ H_3N_2 + 2HO.$$

(7) "(*a*) + urea − $3H_2O$ = uric acid."



which, being fairly interpreted, means:—Tartronyl urea + urea − 4HO = uric acid. Thus:—

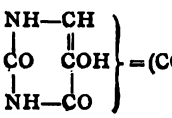
$$(CO)_2\ 6\ 1\ 6\ H_3N_2 + (CO)_2H_4N_2 = (CO)_4C_6H_1O_6H_7N_4\ (a)$$
$$-2HO = (CO)_2Cy\ 6\ 1\ 6\ H_5N_3\ (b)$$
$$-2HO = Cy_2\ 6\ 1\ 6\ H_3N_2\ (c)$$

(*a*) the normal di-ureide, (*b*) pseudo-uric acid, and (*c*) = the ultimate, uric acid.

In the early part of 1888 M. Behrend notated tartronyl urea (*a*) without the 2HO:—

$$CO\langle\begin{matrix}NH\cdot C(OH)\\ NH\cdot C\text{——}\end{matrix}\rangle C\cdot OH = (CO)_2\ (6\ 1\ 6)\ H_3N_2,$$

calling it iso-dialuric acid, and that it crystallises with 4HO, two passing off at 100°, and the remainder at 150°; also that his present iso-barbituric acid (malonyl urea)—



$$= (CO)_2\ (6\ 1\ 4)\ H_3N_2.$$

was then—

$$CO\langle\begin{matrix}NH\cdot CH\\ NH\cdot CO\end{matrix}\rangle C\cdot OH,$$

"iso-barbituric acid is the ureide of dihydroxyacrylic acid."

This curious adherence to old terms and ideas certainly needs further elucidation.

I propose shortly to moot the bearing of all this upon the future synthesis of the vegetable alkaloid caffeine.

Wokingham Road, Reading
May 25, 1889.

WALNUT OIL.

By THOMAS T. P. BRUCE WARREN.

This oil, which I obtained from the fully ripened nut of the *Juglans regia*, has so many excellent properties especially for mixing with artists' colours for fine art work, that I am surprised at the small amount of information available on this interesting oil.

Walnut oil is largely used for adulterating olive oil, and to compensate for its high iodine absorption it is mixed with pure lard oil olein, which also retards the thickening effect due to oxidation. The marc left on expression of the oil is said to be largely used in the manufacture of chocolate. Many people, I am told, prefer walnut oil to olive oil for cooking purposes.

The value of this oil for out-door work has been given me by a friend who used it for painting the verandas and jalousies of his house (near Como, Italy) some twenty years ago, and which have not required painting since. In this country, at least, walnut oil is beyond the reach of the general painter, and I do not know that the pure oil is to be obtained as a commercial article, even on a small scale.

It was in examining the properties of this and other oils, used as adulterants of olive oil, that I was obliged to prepare them so as to be sure of getting them in a reliable condition as regards purity. The walnuts were harvested in the autumn of 1887, and kept in a dry airy room until the following March. The kernels had shrunk up and contracted a disagreeable acrid taste, so familiar with old olive oil, in which this has been used as an adulterant. Most oxidised oils, especially cotton-seed oil, reveal a similar acrid taste, but walnut oil has, in addition, an unmistakable increase in viscosity. The nuts were opened and the kernels thrown into warm water, so as to loosen the epidermis; they were then rubbed in a coarse towel, so as to blanch them. The decorticated nuts were wiped dry and rubbed to a smooth paste in a marble mortar. The paste was first digested in CS_2, then placed in a percolator and exhausted with the same solvent, which was evaporated off. The yield of oil was small, but probably, if the nuts had been left to fully ripen on the trees without knocking them off the yield might have been greater. It is by no means im-

probable that oxidation may have rendered a portion of the oil insoluble. The decorticated kernels gave a perfectly sweet, inodorous, and almost colourless oil, which rapidly thickens to an almost colourless, transparent, and perfectly elastic skin or film, which does not darken or crack easily by age. These are properties which, for fine art painting, might be of great value in preserving the tinctorial purity and freshness of pigments.

Sulphur chloride gives a perfectly white product with the fresh oil, but, when oxidised, the product is very dark, almost black. The iodine absorption of the fresh oil thus obtained is very high, but falls rapidly by oxidation or blowing. A curious fact has been disclosed with reference to the oxidation of this and similar oils. If such an oil be mixed with lard oil, olive oil, or sperm oil, it thickens by oxidation but is perfectly soluble. Such a mixture is largely used in weaving or spinning. Commercial samples of linseed oil, when cold drawn, have a much higher iodine absorption, probably due to the same cause. Oils extracted by CS_2 are very much higher than the same oils, especially if hot pressed.

THE FREE CAUSTIC ALKALI OF SOAP.

By J. A. WILSON.

In a previous note on the same subject in the Chemical News (vol. lix., p. 221) I pointed out that there is a source of error in the spirit method, and this error is due to the simultaneous presence of free alkali and free fat or oil.

When high class soaps are analysed, containing no free glycerides, the spirit method gives very accurate results, but any analyst who has to deal with soaps of any quality, and made in the most imperfect manner, will find the alcohol process perplexing. Hence I have no hesitation in saying that the determination of free caustic alkali in some soaps is one of the *most difficult problems* met with in practice. The conditions necessary to ensure the stability of the soap (*i.e.*, the decomposition into an acid soap and free caustic alkali) are just those conditions necessary to ensure the absolute saponification of the *glycerides* by the *free caustic alkali present*. To any expert in soap analysis the presence of free alkali and glycerides in the sample simultaneously is easily seen; on the addition of alcohol with phenolphthalein the colour goes deep, then gradually fades and may disappear altogether.

The method depending on insolubility of soap in strong brine has been proved to give the most inaccurate results, whilst that depending on precipitation of the alkali by carbonic dioxide gas, the solvent for the soap being alcohol, gives the same conditions necessary for complete saponification as stated above; hence this process is of no use. It is necessary to bear these facts in mind in these days, when we hear so much about the absence of free alkali in certain soaps.

In using the alcohol process for determining free caustic alkali it is necessary to use nearly or, better, absolute alcohol and to conduct the operation with the least possible access of air; moreover, the alcohol should be used largely and in due regard to the percentage of water in the soap.

In these cases, on account of the presence of free fat, the alcohol process must be abandoned if good results are required, and better state the results in this form:—

Alkali in Total, %. Alkali combined with Fatty Acids, %.

If the alkali existing as silicate and carbonate be very carefully determined some idea may be gained of the alkali actually present as sodium hydrate. Supposing palmnut or cocoanut oil to have been used in the fabrication of the soap, the determination of the Na_2O required to neutralise the fatty acids becomes quite inaccurate, owing to the solubility of the lower fatty acids, hence another complication arises.

In order to show the differences between the above methods let me quote a few analyses of mine:—

Nature of the Sample.	Alkali (Na_2O) by Titration.	Alkali by Titration of the Insoluble Fatty Acids.	Alkali by Alcohol Test.
	Per Cent.		
1. Palm oil Soap, Cold Process..	5·00	4·59	0·00
2. Highly Watered Soap from Bone-fat.. ..	3·51	·71	0·31
3. Palm oil Soap similar to No. 1	5·61	5·39	0·00
4. Common Soap for Calico-printers	6·95	6·31	·38
5. Soap from Tallow and Cocoanut Oil	3·59	2·52	0·107
6. Washing Soap sold in North of England	7·33	7·70	0·017

Finally, as interesting, let me notice the article sold for calico-printers' use, known as soluble oil, which is made from castor oil, consisting therefore of the soda salt of ricinoleic acid. This material is required to be as neutral as possible; hence some makers, after saponification, add hydric chloride to neutralise the excess of alkali, which of course is overstepped, and free fatty acid results. Its usual composition is—

Free fatty acid as ricinoleic acid	4·75 per cent.
Total fatty acids	20·50 ,,
Total alkali..	1·67 ,,

On decomposition of this soap with subsequent titration of the washed fatty acids the number of c.c. of alkali used for neutralisation must be corrected by that required to neutralise the free fatty acids. Samples No. 1 and 3 in the table contained matured glycerides easily detected as previously mentioned. That the figure 0·31 per cent, corresponding to soap No. 2, is incorrect, was proved by estimation of the carbonate and silicate in the soap. The last soap in the table actually gave results higher in the third column than in the total column. The analysis especially, as in the others, was conducted most carefully with identical results. Accordingly, I sent a sample from the same to a well-known analyst, who certified as follows:—Alkali as soap, 7·66; alkali in total, 7·51; free alkali by alcohol, 0·02.

It is thus seen that he got results agreeing with mine in the main question, although he got higher results for the direct titration, usually stated as total. These results seem inexplicable, since free fat cannot possibly have any influence. That the estimation of *free caustic alkali* in soap is not so *easy* as is generally supposed will, I think, be admitted.

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AN AUTOMATIC FUMIGATOR.

By H. N. WARREN, Research Analyst.

This form of apparatus is specially indicated both for scientific and commercial purposes, in the former ranking far superior to any form of apparatus designed for the purpose of evolving sulphurous anhydride, the usual method employed in the laboratory being that of decomposing the strongest oil of vitriol either by the aid of metallic copper or ordinary wood-charcoal contained in a flask or suitable apparatus, and applying a continued

heat. Both these substances, however, present considerable drawbacks, the copper in the first instance forming with the strong acid a difficultly soluble salt, causes an annoyance both by surrounding the remaining metal by incrustation, and thus retarding further action, or seriously endangering a fracture of the vessel by incessant bumping. In using the new apparatus, a small dish containing pieces of ordinary roll sulphur after being well lighted, which is best performed by applying a heated iron to the same, is introduced with its contents into a metallic draught, or furnace piece, and a dome with its chimney projection, which is composed either of glass or metal, placed directly over it; a strong draught is at once formed, and the combustion of the sulphur is maintained until the whole is consumed, thus liberating a plentiful supply of sulphur dioxide. By connecting a tube or metallic pipe, as the case may be, bent at right angles with the projecting chimney, and terminating with a refrigerative worm surrounded by a powerful freezing-mixture, a large quantity of liquid sulphurous anhydride may be speedily manufactured, thus rendering the apparatus a useful piece for the lecture table. By connecting with the chimney projection a metallic vane-shaped cap, which is intended to distribute or to allow of the gas intermixing more uniformly with the atmosphere when desired, the apparatus at once furnishes a most efficient fumigator or deodoriser, being also applicable for bleaching purposes.

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THE TERRESTRIAL ORIGIN OF THE OXYGEN RAYS IN THE SOLAR SPECTRUM.

By J. JANSSEN.

M. Eiffel having placed the tower in the Champ de Mars at the author's disposal for the experiments and observations which he wished to institute there, he has utilised the powerful source of light installed there for certain studies of the terrestrial spectrum, with especial reference to the origin of the oxygen rays in the solar spectrum.

It is now known that there exist in the solar spectrum several groups of rays due to the oxygen contained in our atmosphere. But it may be asked if these groups are due exclusively to the action of our atmosphere, and if the sun's atmosphere takes no part in them at all, or, if their origin is twofold; in a word, are they purely terrestrial or terrestrial-solar?

To decide this question several methods are possible. One of the most certain is that of vibrations, the origin of which may be traced to the fine conception of M. Fizeau, and which has been applied by M. Thollon, and improved by M. Cornu. In the present case, however, its application would seem to be very difficult.

We may also observe the decrease of intensity which the groups undergo as we rise in the atmosphere. By the most careful comparisons, and by extended observations, we may judge if the decrease in the intensity of the rays warrants us in inferring their complete disappearance at the bounderies of the atmosphere. This is the method employed in the last expedition to the ridge of Mont Blanc (Grands Mulets). Or we may proceed by a comparison of equality; arranging a powerful light, with a continuous spectrum, at a distance from the instrument, such that the atmospheric stratum traversed may represent the action of the earth's atmosphere upon the sun's rays about the zenith.

These conditions are very happily realised by the respective positions of the Eiffel tower and the observatory of Meudon. The intervening distance is about 7700 metres, which represents approximately the thickness of an atmosphere, having the same weight as the terrestrial atmosphere, and a density which is uniform and equal to that of the atmospheric stratum near the sun. Besides the considerable power of the luminous apparatus installed at the summit of the tower permitted the use of the instrument which the author had employed at Meudon and on the Grands Mulets for the sun. He has also used a collecting-lens before the slit, so as to give the spectrum an intensity comparable to that of the solar spectrum in the same instrument. With these arrangements the spectrum appeared extremely bright. The field extended beyond A. The group B appeared as intense as with the summer sun at noon. The group A was also strongly manifest. Other groups were also distinguished, especially that of watery vapour; their intensity seemed to agree with the hygrometric condition of the atmospheric stratum traversed.

The author wished to study the oxygen groups with the great spectrometer of MM. Brunner and with M. Rowland's grating, but the limited time during which the light was supplied did not permit.

No oxygen band appeared in the visible spectrum. Still, the thickness of the stratum of oxygen traversed was equivalent to a column of more than 260 metres of oxygen, at a pressure of six atmospheres. This shows that for oxygen the rays follow quite a different law from the bands. Whilst for the rays the recent experiment shows that it seems indifferent whether we use a column of gas of constant density or a column equivalent in weight but of variable density; for the bands, on the contrary, the absorption taking place according to the square of the density, there would be required on the surface of the sun an atmospheric thickness of more than 50 kilometres for their production.

M. Janssen considers his experiment as merely supplying an additional fact which requires to be fixed with precision and developed. The height at which the tower of the Champ de Mars enables the luminous focus to be placed, and the power of this focus, promises us further experiments of high interest.—*Comptes Rendus*, vol. cviii., p. 1035.

A METHOD FOR THE DETECTION OF CHLORINE, BROMINE, IODINE, AND SULPHUR IN ORGANIC COMPOUNDS.

By CHARLES W. MARSH.

In testing for sulphur according to Schönn* by heating an organic substance with metallic sodium in a closed tube, dissolving the sodium sulphide formed in water, and adding a solution of sodium nitroprusside, the inconvenience of working with sodium and the precautions necessary in heating the sodium and substance and in adding water to the contents of the tube led the writer to look for another metal to replace the sodium. This metal, when heated with organic bodies, should decompose them and combine with the halogens and sulphur, or, if the substance were decomposed by heat, would enter into like combination.

Magnesium in fine powder has also been recommended by Schonn,† but only for the estimation of sulphur. He heats the substance with powdered magnesium in a hard glass tube, allows it to cool, adds a little water, and heats. The liquid is filtered and a solution of sodium nitroprusside added, and this reacts for sulphur by giving a reddish violet colouration.

Powdered zinc having the property of decomposing organic substances when heated with them, it seemed that this might be a ready substance to decompose organic bodies, and at the same time to unite with the halogens to form chloride, bromide, or iodide, as the case

* *Zeit. Anal. Chem.*, viii., 52
† *Ibid.*, viii., 398.

might be, all of which are soluble in water. From the water solution the corresponding silver salt would be precipitated, which would aid to identify the halogen in the substance treated.

The substances containing sulphur in any form of combination would, on heating with zinc, form zinc sulphide. This could be decomposed by the addition of hydrochloric acid direct to the tube containing the zinc and charred residue of the organic substance, if any, and the sulphuretted hydrogen gas then tested for at the mouth of the tube by means of a narrow slip of filter-paper moistened with lead acetate solution.

The method of procedure outlined was tried on many organic substances containing chlorine, bromine, iodine, and sulphur, and gave the expected results. Several organic substances containing no chlorine, bromine, or iodine, were treated in the same manner, and a white precipitate invariably appeared on the addition of nitric acid and silver nitrate solution. The distilled water was tested, but gave no reaction for chlorine. A small quantity of zinc was shaken with water, the liquid poured on a filter, and to the filtrate nitric acid and silver nitrate solution were added, and immediately a white precipitate appeared, which was soluble in ammonium hydrate and re-precipitated by nitric acid, showing the presence of a large quantity of chlorine in the zinc. The test for sulphur was made as described, a brown colour being obtained on the lead acetate paper, showing the presence of a small amount of sulphur. The zinc was some used in the organic laboratory work, and came in the form of powder. As the zinc used contained chlorine and sulphur, the tests already made were valueless.

Another sample of fine zinc used in the reduction of ferric iron solutions was treated for chlorine and gave no reaction. It also gave no reaction for sulphur. This zinc comes in a spherical form, the diameters of which are mostly half a millimetre. The experiments made with the impure zinc were repeated with the pure sample, and also on several other compounds. The test on substances containing no chlorine, bromine, iodine, nor sulphur were made, and in no case was a distinct reaction obtained. In but one case an opalescence appeared after the addition of nitric acid and silver nitrate solution, while in all the others the solution remained perfectly clear. No trace of sulphur could be detected. This proved that the decomposition of organic substances on heating would not give reactions similar to the ones characteristic of the elements sought.

The substance was heated in about the same manner in every case, with a few exceptions, which will be described. Many of the tests were made in small hard-glass closed tubes, such as are used in blowpipe analysis, having an internal diameter of five millimetres and a length of sixty millimetres. Four-inch test tubes were found to give as satisfactory results.

The exact details of manipulation are as follows:—

The substance is first introduced into the tube and then the zinc is added in about equal volume. They are intimately mixed by shaking. The tube is held in a slanting position, with the lower end in the flame, and heated slowly. In many cases the substance volatilises, condenses in the upper end of the tube, and runs down upon the hot zinc, when it is decomposed. In others it carbonises and a watery coloured liquid distils.

If combustible gases or vapours are given off, they are lighted. It is better not to heat the tube red hot, for in that case the zinc would melt to a globule and inclose some of the zinc salt formed. At the same time the zinc chloride, bromide, and iodide would be volatilised and thus cause a loss. Zinc sulphide is not volatile.

If a liquid is under examination it is better to use a test-tube, as the mouth is wider. The liquid is first added to the test-tube, which moistens the sides, so that when the zinc is added it will adhere to the inner walls and some remain near the mouth. The test-tube, held in a wooden holder, is slightly heated, and the vapours, if inflammable, are ignited, while the tube is held in a position nearly horizontal. The heat is so regulated that the flame will be as small as possible, and will tend to burn down in the tube and there act upon the zinc adhering to the sides. With the liquids methyl iodide, ethyl iodide, and carbon disulphide, this was the only method by which reactions for iodine and sulphur could be obtained. With para-dichlor-benzene this last method gave good results, whereas the general method of heating gave no reaction for chlorine.

After heating with zinc the residue in the tube is cooled and treated as follows:—

For Chlorine.—About one cubic centimetre of distilled water is added direct to the test-tube, the whole shaken and allowed to stand, while a small filter is fitted to a funnel. The liquid is now poured on the filter and caught in a short test-tube placed underneath. The filtrate is acidified with nitric acid and a solution of silver nitrate added. A white precipitate of silver chloride, soluble in ammonium hydrate and re-precipitated by nitric acid, was obtained from the following substances tested:—

Liquids.—Chloroform, acetyl chloride, ethylene chloride, allyl chloride.

Solids.—Mono-chlor-crotonic acid, para-dichlor-benzene, trichlor-phenol.

For Bromine.—The contents of the tube are treated with water and filtered, as in the test for chlorine. The filtrate is divided into two parts. In one part nitric acid and silver nitrate solution are added, when the light yellow precipitate of silver bromide appears. To the other part of the filtrate nitric acid is added and a few drops of carbon disulphide. The carbon disulphide is coloured brown from the bromine liberated. In several cases the precipitate of silver bromide was very slight, but in every case the carbon disulphide was strongly coloured.

The following substances gave the reactions described:—

Liquids.—Acetyl bromide, amyl bromide, isobutyl-bromide, brom-toluene.

Solids.—Tribrom-aniline, ortho-nitro-dibrom-phenyl-propionic acid, dibrom-benzene, mono-brom-camphor, dibrom-camphor, eosine, dibrom-gallein, dibrom-anthraquinone, dibrom-anthracene.

For Iodine.—The filtrate is divided and treated as in the case of bromine. Yellow silver iodide is obtained in the first instance, and the carbon disulphide coloured violet by the iodine freed from the zinc by the nitric acid in the second.

Iodine was thus detected in the following substances:—

Liquids.—*Methyl iodide, ethyl iodide, allyl iodide, isobutyl iodide.

Solids.—Iodoform.

For Sulphur.—To the tube containing the residue after heating the substance with zinc a few drops of hydrochloric acid are added, and the hydrogen sulphide generated identified as it escapes from the mouth of the tube by filter-paper moistened with lead acetate solution. The paper is turned brown almost immediately. There is no necessity for heating the tube. The compounds in the list gave distinct reactions.

Liquids.—Carbon disulphide, allyl mustard oil, ethyl sulphocyanate.

Solids.—Sulpho-urea, potassium amyl sulphate, sulphanilic acid, ammonium diphenyl-amidazo-benzene sulphonate, saccharin, sodium beta-naphthol-disulphonate, mono-sodium anthraquinone sulphonate, morphine sulphate.

It is claimed that, by using the process described, chlorine, bromine, iodine, and sulphur can be accurately and rapidly detected in organic compounds by the use of

* The liquid iodides used were more or less decomposed and coloured by iodine set free. In order to work upon undecomposed chemicals, they were each separately shaken with potassium hydrate solution, to take up the iodine, and the resulting colourless alcoholic iodide was repeatedly washed with water. The iodides thus treated were used for the experiments.

apparatus and chemicals ordinarily found in chemical laboratories.—*American Chemical Journal*, vol. xi., No. 4.

ALUMINIUM.*

By Sir HENRY ROSCOE, M.P., D.C.L., LL.D., V.P.R.S.

Chemists of many lands have contributed to our knowledge of the metal aluminium. Davy, in 1807, tried in vain to reduce alumina by means of the electric current. Oerstedt, the Dane, in 1824, pointed out that the metal could be obtained by treating the chloride with an alkali metal; this was accomplished in Germany by Wöhler in 1827, and more completely in 1845, whilst in 1854, Bunsen showed how the metal can be obtained by electrolysis. But it is to France, by the hands of Henri Ste.-Claire Deville, in the same year, that the honour belongs of having first prepared aluminium in a state of purity, and of obtaining it on a scale which enabled its valuable properties to be recognised and made available, and the bar of "silver-white metal from clay" was one of the chemical wonders in the first Paris Exhibition of 1855. Now England and America step in, and I have this evening to relate the important changes which further investigation has effected in the metallurgy of aluminium. The process suggested by Oerstedt, carried out by Wöhler, and modified by Deville, remains in principle unchanged. The metal is prepared, as before, by a reduction of the double chloride of aluminium and sodium, by means of metallic sodium in presence of cryolite; and it is therefore not so much a description of a new reaction as of improvements of old ones of which I have to speak.

I may perhaps be allowed to remind my hearers that more than 33 years ago, Mr. Barlow, then secretary to the Institution, delivered a discourse in the presence of M. Deville on the properties and mode of preparation of aluminium, then a novelty. He stated that the metal was then sold at the rate of £3 per ounce, and the exhibition of a small ingot, cast in the laboratory by M. Deville, was considered remarkable. As indicating the progress since made, I may remark that the metal is now sold at 20s. per lb., and manufactured by the ton, by the Aluminium Company, at their works at Oldbury, near Birmingham. The improvements which have been made in this manufacture by the zeal and energy of Mr. Castner, an American metallurgist, are of so important a character, that the process may properly be termed the Deville-Castner process.

The production of aluminium previous to 1887, probably did not exceed 10,000 lbs. per annum, whilst the price at that time was very high. To attain even this production required that at least 100,000 lbs. of double chloride, and 40,000 lbs of sodium should be manufactured annually. From these figures an idea of the magnitude of the undertaking assumed by the Aluminium Company may be estimated, when we learn that they erected works having an annual producing capacity of 100,000 lbs. of aluminium. To accomplish this, required not only that at least 400,000 lbs. of sodium, 800,000 lbs. of chlorine, and 1,000,000 lbs. of double chloride, should be annually manufactured, but in addition that each of these materials should be produced at a very low cost, in order to enable the metal to be sold at 20s. per lb.

The works now cover a space of nearly five acres. They are divided into five separate departments, viz., 1st, sodium; 2nd, chlorine; 3rd, chloride; 4th, aluminium; and 5th, foundry, rolling, wire mills, &c.

In each department an accurate account is kept of the production each day, the amount of material used, the different furnaces and apparatus in operation, &c. In this manner it has been found possible to ascertain each day exactly how the different processes are progressing, and what effect any modification has, either on cost, quantity, or quality of product. By this means a complicated chemical process is reduced to a series of very simple operations, so that whilst the processes are apparently complicated and difficult to carry out successfully, this is not the case now that the details connected with the manufacture have been perfected, and each operation carried on quite independently until the final materials are brought together for the production of the aluminium.

Manufacture of Sodium.

The first improvement occurs in the manufacture of sodium by what is known as the "Castner Process." The successful working of this process marks an era in the production of sodium, as it not only has greatly cheapened the metal, but has enabled the manufacture to be carried out upon a very large scale with little or no danger. Practically, the process consists in heating fused caustic soda in contact with carbon whilst the former substance is in a perfectly liquid condition. By the process in vogue before the introduction of this method, it was always deemed necessary that special means should be taken to guard against actual fusion of the mixed charges, which, if it were to take place, would to a large extent allow the alkali and reducing material to separate. Thus, having an infusible charge to heat, requiring the employment of a very high temperatue for its decomposition, the iron vessels must be of small circumference to allow the penetration of the heat to the centre of the charge without actually melting the vessel in which the materials are heated. By the new process, owing to the alkali being in a fused or perfectly liquid condition in contact directly with carbon, the necessity of this is avoided, and consequently, the reduction can be carried on in large vessels at a comparatively low temperature. The reaction taking place may be expressed as follows:—

$$3NaHO + C = Na_2CO_3 + 3H + Na.$$

The vessels in which the charges of alkali and reducing material are heated are of egg-shaped pattern, about 18 inches in width at their widest part and about 3 feet high, and are made in two portions, the lower one being actually in the form of a crucible, while the upper one is provided with an unright stem and a protruding hollow arm. This part of the apparatus is known as the cover. In commencing the operation, these covers are raised in the heated furnace through apertures provided in the floor of the heated chamber, and are then fastened in their place by an attachment adjusted to the stem; the hollow arm extends outside the furnace. Directly below each aperture in the bottom of the furnace are situated the hydraulic lifts, attached to the top of which are the platforms upon which are placed the crucibles to be raised into the furnace. Attached to the hydraulic lifts are the usual reversing valves for lowering or raising, and the platform is of such a size as, when raised, completely to fill the bottom aperture of the furnace. The charged crucible, being placed upon the platform, is raised into its position, the edges meeting those of the cover, forming an air-tight joint which prevents the escape of gas and vapour from the vessel during reduction, except by the hollow arm provided for this purpose. The natural expansion of the iron vessels is accommodated by the water-pressure in the hydraulic lifts, so that the joint of the cover and crucible are not disturbed until it is intended to lower the lift for the purpose of removing the crucible.

The length of time required for the first operation of reduction and distillation is about two hours. At the end of this time the crucibles are lowered, taken from the platforms by a large pair of tongs on wheels, carried to a dumping pit, and thrown on their side. The residue is cleaned out, and the hot pot, being again gripped by the tongs, is taken back to the furnace. On its way, the charge of alkali and reducing material is thrown in. It is again placed on the lift and raised in position against

* A Lecture delivered at the Royal Institution of Great Britain, May 3, 1889.

the edges of the cover. The time consumed in making the change is one and a half minutes, and it only requires about seven minutes to draw, empty, recharge, and replace the five crucibles in each furnace. In this manner the crucibles retain the greater amount of their heat, so that the operation of reduction and distillation now only requires one hour and ten minutes. Each of the four furnaces, of five crucibles each, when in operation, are drawn alternately, so that the process is carried on night and day.

Attached to the protruding hollow arm from the cover are the condensers, which are of a peculiar pattern specially adapted to this process, being quite different from those formerly used. They are about 5 inches in diameter, and nearly 3 feet long, and have a small opening in the bottom about 20 inches from the nozzle. The bottom of these condensers is so inclined that the metal condensed from the vapour issuing from the crucible during reduction, flows down and out into a small pot placed directly below this opening. The uncondensed gases escape from the condenser at the further end, and burn with the characteristic sodium flame. The condensers are also provided with a small hinged door at the further end, by means of which the workmen from time to time may look in to observe how the distillation is progressing. Previous to drawing the crucibles from the furnace for the purpose of emptying and recharging, the small pots each containing the distilled metal are removed, and empty ones substituted. Those removed each contain on an average about 6 lbs. of metal, and are taken directly to the sodium casting shop, where it is melted and cast, either into large bars ready to be used for making aluminium, or in smaller sticks to be sold.

Special care is taken to keep the temperature of the furnaces at about 1000° C., and the gas and air valves are carefully regulated, so as to maintain as even a temperature as possible. The covers remain in the furnace from Sunday night to Saturday afternoon, and the crucibles are kept in use until they are worn out, when new ones are substituted without interrupting the general running of the furnace. A furnace in operation requires 250 lbs. of caustic soda every one hour and ten minutes, and yields in the same time 30 lbs. of sodium, and about 240 lbs. of crude carbonate of soda. With the four furnaces at work 120 lbs. of sodium can be made every seventy minutes, or over a ton in the twenty-four hours. The residual carbonate, on treatment with lime in the usual manner, yields two-thirds of the original amount of caustic operated upon. The sodium, after being cast, is saturated with kerosene oil, and stored in large tanks holding several tons, placed in rooms specially designed both for security against either fire or water.

Chlorine Manufacture.

This part of the works is connected with the adjacent works of Messrs. Chance Bros. by a large gutta-percha pipe, by means of which from time to time hydrochloric acid is supplied direct into the large storage cisterns, from which it is used as desired for making the chlorine. For the preparation of the chlorine gas needed in making the chloride, the usual method is employed: that is, hydrochloric acid and manganese dioxide are heated together when chlorine gas is evolved with effervescence, and is led away by earthenware and lead pipes to large lead-lined gasometers, where it is stored.

The materials for the generation of the chlorine are brought together in large tanks, or stills, built up out of great sandstone slabs, having rubber joints, and the heating is effected by the injection of steam. The evolution of gas, at first rapid, becomes gradually slower, and at last stops; the hydrochloric acid and manganese dioxide being converted into chlorine and manganous chloride. This last compound remains dissolved in the "spent still liquor," and is re-converted into manganese dioxide, to be used over again, by Weldon's Manganese Recovery Process. Owing to the difficulty of keeping up a regular supply of chlorine under a constant pressure directly from the stills, in order that the quantity passed into the sixty different retorts in which the double chloride is made can be regulated and fed as desired, four large gasometers were erected. Each of these is capable of holding 1000 cubic feet of gas, and is completely lined with lead, as are all the connecting mains, &c., this being the only available metal which withstands the corrosive action of chlorine. The gasometers are filled in turn from the stills, the chlorine consumed being taken direct from a gasometer under a regular pressure until it is exhausted, the valves being changed, the supply is taken from another holder, the emptied one being re-filled from the still.

Manufacture of the Double Chloride.

Twelve large regenerative gas furnaces are used for heating, and in each of these are fixed five horizontal fire-clay retorts about 10 ft. in length, into which the mixture for making the double chloride is placed. These furnaces have been built in two rows, six on a side, the clear passage-way down the centre of the building, which is about 250 ft. long, being 50 ft. in width. Above this central passage is the staging, carrying the large lead-mains for the supply of the chlorine coming from the gasometers. Opposite each retort and attached to the main are situated the regulating valves, connected with lead and earthenware pipes, for the regulation and passage of the chlorine to each retort. The valves are of peculiar design, and have been so constructed that the chlorine is made to pass through a certain depth of liquid, which not only, by opposing a certain pressure, allows a known quantity of gas to pass in a given time, but also prevents any return from the retort into the main, should an increase of pressure be suddenly developed in the retorts.

The mixture with which the retorts are charged is made by grinding together hydrate of alumina, salt, and charcoal. This mixture is then moistened with water, which partially dissolves the salt, and thrown into a pug-mill of the usual type for making drain-pipes, excepting that the mass is forced out into solid cylindrical lengths upon a platform alongside of which a workman is stationed with a large knife, by means of which the material is cut into lengths of about three inches each. These are then piled on top of the large furnaces to dry. In a few hours they have sufficiently hardened to allow of their being handled. They are then transferred to large wagons, and are ready to be used in charging the retorts.

The success of this process is in a great measure dependent, 1st, on the proportionate mixture of materials; 2nd, on the temperature of the furnace; 3rd, on the quantity of chlorine introduced in a given time; and 4th, on the actual construction of the retorts. I am, however, not at liberty to discuss the details of this part of the process, which have only a commercial interest. In carrying on the operation the furnaces or retorts, when at the proper temperature, are charged by throwing in the balls until they are quite full, the fronts are then sealed up, and the charge allowed to remain undisturbed for about four hours, during which time the water of the alumina hydrate is completely expelled. At the end of this time the valves on the chlorine main are opened, and the gas is allowed to pass into the charged retorts. In the rear of each retort, and connected therewith by means of an earthenware pipe, are the condenser boxes which are built in brick. These boxes are provided with openings or doors, and also with earthenware pipes, connected with a small flue for carrying off the uncondensed vapours to the large chimney. At first the chlorine passed into each retort is all absorbed by the charge, and only carbonic oxide escapes into the open boxes, where it burns. After a certain time, however, dense fumes are evolved, and the boxes are then closed, while the connecting pipe between the box and the small flue serves to carry off the uncondensed vapours to the chimney.

The reaction which takes place is as follows:—

$$Al_2O_3+2NaCl+3C+6Cl=2AlCl_3NaCl+3CO.$$

The chlorine is passed in for about seventy-two hours in varying quantity, the boxes at the back being opened from time to time by the workmen to ascertain the progress of the distillation. At the end of the time mentioned the chlorine valves are closed and the boxes at the back of the furnace are all thrown open. The crude double chloride, as distilled from the retorts, condenses in the connecting pipe and trickles down into the boxes, where it solidifies in large irregular masses. The yield from a bench of five retorts will average from 1600 to 1800 lbs., which is not far from the theoretical quantity. After the removal of the crude chloride from the condenser boxes the retorts are opened at their charging end, and the residue, which consists of a small quantity of alumina, charcoal, and salt, is raked out and re-mixed in certain proportions with fresh material, to be used over again. The furnace is immediately re-charged and the same operations repeated, so that from each furnace upwards of 3500 lbs. of chloride are obtained weekly. With ten of the twelve furnaces always at work the plant is easily capable of producing 30,000 lbs. of chloride per week, or 1,500,000 lbs. per annum.

Owing to the presence of iron, both in the materials used (viz., charcoal, alumina, &c.) and in the fire-clay composing the retorts, the distilled chloride always contains a varying proportion of this metal in the form of ferrous and ferric chlorides. When it is remembered that it requires 10 lbs. of this chloride to produce 1 lb. of aluminium by reduction, it will be quite apparent how materially a very small percentage of iron in the chloride will influence the quality of the resulting metal. I may say that, exercising the utmost care as to the purity of the alumina and the charcoal used, and after having the retorts made of special fire-clay containing only a very small percentage of iron, it was found almost impossible to produce upon a large scale a chloride containing less than 0·3 per cent of iron.

This crude double chloride, as it is now called at the works, is highly deliquescent, and varies in colour from a light yellow to a dark red. The variation in colour is not so much due to the varying percentage of iron contained as to the relative proportion of ferric or ferrous chlorides present, and although a sample may be either very dark or quite light, it may still contain only a small percentage of iron if it be present as ferric salt, or a very large percentage if it is in the ferrous condition. Even when exercising all possible precautions, the average analysis of the crude double chloride shows about 0·4 per cent of iron. The metal subsequently made from this chloride, therefore, never contained much less than about 5 per cent of iron, and, as this quantity greatly injures the capacity of aluminium for drawing into wire, rolling, &c., the metal thus obtained required to be refined. This was successfully accomplished by Mr. Castner and his able assistant Mr. Cullen, and for some time all the metal made was refined, the iron being lowered to about 2 per cent.

The process, however, was difficult to carry out, and required careful manipulation, but as it then seemed the only remedy for effectively removing the iron, it was adopted and carried on for some time quite successfully, until another invention of Mr. Castner rendered it totally unnecessary. This consisted in purifying the double chloride before reduction. I cannot now explain this process, but I am able to show some of the product. This purified chloride, or pure double chloride, is, as you see, quite white, and is far less deliquescent than the crude, so that it is quite reasonable to infer that this most undesirable property is greatly due to the former presence of iron chlorides. I have seen large quantities containing upwards of 1¼ per cent of iron, or 150 lbs. to 10,000 of the chloride, completely purified from iron in a few minutes, so that, whilst the substance before treatment was wholly unfit for the preparation of aluminium, owing to the presence of iron, the result was, like the sample exhibited, a mass containing only 1 lb. of iron in 10,000, or 0·01 per cent. The process is extremely simple, and adds little or no appreciable cost to the final product. After treatment, this pure chloride is melted in large iron pots and run into drums similar to those used for storing caustic soda. As far as I am aware it was generally believed to be an impossibility to remove the iron from anhydrous double chloride of aluminium and sodium, and few, if any, chemists, have ever seen a pure white double chloride.

Aluminium Manufacture.

I now come to the final stage of the process, viz., the reduction of the pure double chloride by sodium. This is effected, not in a tube of Bohemian glass, as shown in Mr. Barlow's lecture in 1856, but in a large reverberatory furnace, having an inclined hearth about six feet square, the inclination being towards the front of the furnace, through which are several openings at different heights. The pure chloride is ground together with cryolite in about the proportions of two to one, and is then carried to a staging erected above the reducing furnace. The sodium, in large slabs or blocks, is run through a machine similar to an ordinary tobacco-cutting machine, where it is cut into small thin slices; it is then also transferred to the staging above the reducing furnace.

Both materials are now thrown into a large revolving drum, when they become thoroughly mixed. The drum being opened and partially turned, the contents drop out into a car on a tramway directly below. The furnace having been raised to the desired temperature, the dampers of the furnace are all closed to prevent the access of air, the heating gas also being shut off. The car is then moved out on the roof of the furnace until it stands directly over the centre of the hearth. The furnace roof is provided with large hoppers, and through these openings the charge is introduced as quickly as possible. The reaction takes place almost immediately, and the whole charge quickly liquefies. At the end of a certain time the heating gas is again introduced and the charge kept at a moderate temperature for about two hours. At the end of this period the furnace is tapped by driving a bar through the lower opening, which has previously been stopped with a fire-clay plug, and the liquid metal run out in a silver stream into moulds placed below the opening. When the metal has all been drawn off, the slag is allowed to run out into small iron wagons and removed. The openings being again plugged up, the furnace is ready for another charge. From each charge, composed of about 1200 lbs. of pure chloride, 600 lbs. of cryolite, and 350 lbs. of sodium, about 115 to 120 lbs. of aluminium is obtained.

The purity of the metal entirely depends upon the purity of the chloride used, and without exercising more than ordinary care the metal tests usually indicate a purity of metal above 99 per cent. On the table is the metal run from a single charge, its weight is 116 lbs., and its composition, as shown by analysis, is 99·2 aluminium, 0·3 silicon, and 0·5 iron. This I believe to be the largest and the purest mass of metal ever made in one operation.

The result of eight or nine charges are laid on one side, and then melted down in the furnace to make a uniform quality, the liquid metal, after a good stirring, being drawn off into moulds. These large ingots, weighing about 60 lbs. each, are sent to the casting shop, there to be melted and cast into the ordinary pigs, or other shapes, as may be required for the making of tubes, sheets, or wire, or else used directly for making alloys of either copper or iron.

The following Table shows approximately the quantity of each material used in the production of one ton of aluminium:—

Metallic sodium	6,300 lbs.
Double chloride	22,400 ,,
Cryolite	8,000 ,,
Coal	8 tons

To produce 6300 lbs. of sodium is required:—

Caustic soda	44,000 lbs.
Carbide made from pitch, 12,000 lbs., and iron turnings, 1000 lbs. ..	7,000 ,,
Crucible castings	2½ tons
Coal	75 ,,

For the production of 22,400 lbs. double chloride is required:—

Common salt	8,000 lbs.
Alumina hydrate	11,000 ,,
Chlorine gas	15,000 ,,
Coal	180 tons

For the production of 15,000 lbs. of chlorine gas is required:—

Hydrochloric acid	180,000 lbs.
Limestone dust	45,000 ,,
Lime	30,000 ,,
Loss of manganese	1,000 ,,

(These figures were rendered more evident by the aid of small blocks, each cut a given size so as to represent the relative weights of the different materials used to produce one unit of aluminium).

It might seem, on looking over the above numbers, as if an extraordinary amount of waste occurred, and as if the production is far below that which ought to be obtained, but a study of the figures will show that this is not the case. I would wish to call attention to one item in particular, viz., fuel, it having been remarked that the consumption of coal must prevent cheap production. I think when it is remembered that coal, such as used at the works, costs only 4s. per ton, while the product is worth £2240 per ton, the cost of coal is not an item of consequence in the cost of production. The total cost of the coal to produce one ton of metal being £50; the actual cost for fuel is less than sixpence for every pound of aluminium produced. The ratio of cost of fuel to value of product is indeed less than is the case in making either iron or steel. In concluding my remarks as to the method of manufacture and the process in general, I may add that I do not think it is too much to expect, in view of the rapid strides already made, that in the future, farther improvements and modifications will enable aluminium to be produced and sold even at a lower price than appears at present possible.

Properties of Aluminium.

In its physical properties aluminium widely differs from all the other metals. Its colour is a beautiful white, with a slight blue tint. The intensity of this colour becomes more apparent when the metal has been worked, or when it contains silicon or iron. The surface may be made to take a very high polish, when the blue tint of the metal becomes manifest, or it may be treated with caustic soda and then nitric acid, which will leave the metal quite white. The extensibility or malleability of aluminium is very high, ranking with gold and silver if the metal be of good quality. It may be beaten out into thin leaf quite as easily as either gold or silver, although it requires more careful annealing.

It is extremely ductile and may be easily drawn, especial care only being required in the annealing.

The excessive sonorousness of aluminium is best shown by example (large suspended bar being struck). Faraday has remarked, after experiments conducted in his laboratory, that the sound produced by an ingot of aluminium is not simple, and one may distinguish the two sounds by turning the vibrating ingot.

After being cast it has about the hardness of pure silver, but may be sensibly hardened by hammering.

Its tensile strength varies between 12 and 14 tons to the inch (test sample which was shown having been broken at 13 tons or 27,000 lbs.), ordinary cast iron being about 8 tons. Comparing the strength of aluminium in relation to its weight, it is equal to steel of 38 tons tensile strength. The specific gravity of cast aluminium is 2·58, but after rolling or hammering this figure is increased to about 2·68.

The specific gravity of aluminium being 1, copper is 3·6, nickel 3·5, silver 4, lead 4·8, gold 7·7.

The fusibility of aluminium has been variously stated as being between that of zinc and silver, or between 600° and 1000° C.

As no reliable information has ever been made public on this subject, my friend Professor Carnelley undertook to determine it. I was aware, from information gained at the works at Oldbury, that a small increase in the percentage of contained iron materially raised its point of fusion, and it has been undoubtedly due to this cause that such wide limits are given for the melting-point. Under these circumstances two samples were forwarded for testing, of which No. 1, containing ½ per cent of iron, had a melting-point of 700° C.; whereas No. 2, containing 5 per cent of iron, does not melt at 700°, and only softens somewhat above that temperature, but undergoes incipient fusion at 730°.

According to Faraday, aluminium ranks very high among metallic conductors of heat and electricity, and he found that it conducted heat better than either silver or copper. The specific heat is also very high, which accounts for length of time required for an ingot of the metal to either melt or get cold after being cast.

Chemically, its properties are well worthy of study.

Air, either wet or dry, has absolutely no effect on aluminium at the ordinary temperature, but this property is only possessed by a very pure quality of metal, and the pure metal in mass undergoes only slight oxidation even at the melting-point of platinum.

Thin leaf, however, when heated in a current of oxygen, burns with a brilliant bluish white light. (Experiment shown). If the metal be pure, water has no effect on it whatever, even at a red heat. Sulphur and its compounds also are without action on it, while, under the same circumstances, nearly all metals would be discoloured with great rapidity. (Experiment shown using silver and aluminium under the same conditions).

Dilute sulphuric acid and nitric acid, both diluted and concentrated, have no effect on it, although it may be dissolved in either hydrochloric acid or caustic alkali. Heated in an atmosphere of chlorine it burns with a vivid light, producing aluminium chloride. (Experiment shown). In connection with the subject it may be of interest to state the true melting-point of the double chloride of aluminium and sodium, which has always been given at 170° to 180° C., but which Mr. Baker, the chemist of the works, finds lies between 125° and 130° C.

Uses of Aluminium.

Its uses, unalloyed, have heretofore been greatly restricted. This is, I believe, alone owing to its former high price, for no metal possessing the properties of aluminium could help coming into larger use if its cost were moderate. Much has been said as to the impossibility of soldering it being against its popular use, but I believe that this difficulty will now soon be overcome. The following are a few of the purposes to which it is at present put:—Telescope tubes, marine glasses, eyeglasses, and sextants, especially on account of its lightness. Fine wire for the making of lace, embroidery, &c. Leaf, in the place of silver leaf, sabre sheaths, sword handles, &c., statuettes, and works of art, jewellery, and delicate physical apparatus, culinary utensils, harness fittings, metallic parts of soldiers' uniforms, dental purposes, surgical instruments, reflectors (it not being tarnished by the products of combustion), photographic apparatus, aëronautical and engineering purposes, and especially for the making of alloys.

Alloys of Aluminium.

The most important alloys of aluminium are those

made with copper. These alloys were first prepared by Dr. Percy, in England, and now give promise of being largely used. The alloy produced by the addition of 10 per cent of aluminium to copper, the maximum amount that can be used to produce a satisfactory alloy, is known as aluminium bronze. Bronzes, however, are made which contain smaller amounts of aluminium, possessing in a degree the valuable properties of the ten per cent bronze. According to the percentage of aluminium up to 10 per cent, the colour varies from red gold to pale yellow. The 10 per cent alloy takes a fine polish, and has the colour of jewellers' gold. The 5 per cent alloy is not quite so hard, the colour being very similar to that of pure gold. I am indebted to Prof. Roberts-Austen for a splendid specimen of crystallised gold, as also for a mould in which the gold at the Mint is usually cast, and in this I have prepared ingots of the 10 and 5 per cent alloy, so that a comparison may be made of the colour of these with a gold ingot cast in the same mould (for the loan of which I have to thank Messrs. Johnson, Matthey, and Co.), all of which are before you.

I have also ingots of the same size, of pure aluminium, from which an idea of the relative weights of gold and aluminium may be obtained.

To arrive at perfection in the making of these alloys, not only is it required that the aluminium used should be of good quality, but also that the copper must be of the very best obtainable. For this purpose only the best brands of Lake Superior copper should be used. Inferior brands of copper or any impurities in the alloy give poor results. The alloys all possess a good colour, polish well, keep their colour far better than all other copper alloys, are extremely malleable and ductile, can be worked either hot or cold, easily engraved, the higher grades have an elasticity exceeding steel, are easily cast into complicated objects, do not lose in re-melting, and are possessed of great strength, dependent, of course, on the purity and percentage of contained aluminium. The 10 per cent alloy, when cast, has a tensile strength of between 70,000 and 80,000 lbs. per square inch, but when hammered or worked, the test exceeds 100,000 lbs. (A sample shown broke at 105,000 lbs.)

An attempt to enumerate either the present uses or the possible future commercial value of these alloys is beyond my present purpose. I may, however, remark that they are not only adapted to take the place of bronze, brass, and steel, but they so far surpass all of those metals, both physically and chemically, as to make their extended use assured. (Sheets, rods, tubes, wire, and ingots shown),

But even a more important use of aluminium seems to be its employment in the iron industry, of which it promises shortly to become a valuable factor, owing to certain effects which it produces when present, even in the most minute proportions. Experiments are now being carried on at numerous iron and steel works, in England, on the Continent, and in America. The results so far attained are greatly at variance, for whilst in the majority of cases the improvements made have encouraged the continuance of the trials, in others the results have not been satisfactory. On this point I would wish to say to those who may contemplate making use of aluminium in this direction, that it would be advisable before trying their experiments to ascertain whether the aluminium alloy they may purchase actually contains any aluminium at all, for some of the so-called aluminium alloys contain little or no aluminium, and this may doubtless account for the negative results obtained. Again, others contain such varying proportions of carbon, silicon, and other impurities, as to render their use highly objectionable.

It seems to be a prevailing idea with some people, that because aluminium is so light compared with iron, that they cannot be directly alloyed, and furthermore, that for the same reason, alloys made by the direct melting together of the two metals would not be equal to an alloy where both metals are reduced together. Now, of course, this is not the case, and the statement has been put forward by those who were only able to make the alloys in one way.

Aluminium added to molten iron and steel lowers their melting-points, consequently increases the fluidity of the metal, and causes it to run easily into moulds and set there, without entrapping air and other gases, which serve to form blow-holes and similar imperfections. It is already used by a large number of steel founders, and seems to render the production of sound steel castings more certain and easy than is otherwise possible.

One of the most remarkable applications of this property which aluminium possesses of lowering the melting-point of iron has been made use of by Mr. Nordenfelt in the production of castings of wrought iron.

Aluminium forms alloys with most other metals, and although each possess peculiar properties which in the future may be utilised, at present they are but little used.

In conclusion, I beg to call your attention to the wood models on the table, one being representative of aluminium, the other aluminium bronze. The originals of these models are now in the Paris Exhibition, each weighing 1000 lbs. With regard to the aluminium bronze, I cannot speak positively, but the block of pure aluminium is undoubtedly the largest casting ever made in this most wonderful metal.

I have to thank the Directors of the Aluminium Company, and especially Mr. Castner, for furnishing me with the interesting series of specimens of raw and manufactured metal for illustrating my discourse.

NOTICES OF BOOKS.

The Chemistry of Chlorophyll. By EDWARD SCHUNCK, Ph.D., F.R.S., F.C.S. (Reprinted from *Annals of Botany*, February, 1889).

NOTWITHSTANDING much elaborate research, the nature of chlorophyll is as yet so imperfectly known that different authorities return discordant answers to the question, what is to be understood by the term? Pelletier and Caventon, its sponsors, consider chlorophyll as simply an organic colouring-matter, like indigo or alizarine. Some chemists define it as the sum of the coloured constituents of green leaves, soluble in alcohol and ether, but insoluble in water. Physiologists have applied the term chlorophyll to "the complex of substances contained in living green cells which take part in the process of assimilation, and of which the colouring matter constitutes a portion." Dr. Schunck, in this investigation, adheres very closely to the definition of Pelletier and Caventon, and means "simply the substance, or, it may be, the mixture of substances, to which the pure green colour of ordinary healthy leaves and other vegetable organs is due."

In speaking of the isolation of chlorophyll the author shows that it is an unstable compound, very sensitive to the action of acids. Hence, Berzelius, Mulder, Morot, and Fremy, who used hydrochloric acid in preparing chlorophyll, obtained and studied decomposition-products.

Arm. Gautier in preparing chlorophyll uses neutral solvents only. Hansen treats the alcoholic extract with caustic lye to saponify fatty matters, the residue being then successively extracted with petroleum ether and with ordinary ether, the pure chlorophyll being finally obtained by crystallisation from a mixture of alcohol and ether. Dr. Schunck, however, cannot accept Hansen's conclusions, as the product obtained, unlike ordinary chlorophyll, is readily soluble in water. He is further led to the conclusion that chlorophyll is modified by the action of alkalies, that it has not yet been obtained in a state of purity, and that in the plant it probably exists in an amorphous state. An approximately pure solution of

chlorophyll may be obtained by mixing the alcoholic extract of grass with twice its volume of water, and agitating with ether. The ether takes up the chlorophyll (though not alone), whilst certain yellow colouring-matters are left in the watery solution.

The solutions of chlorophyll in alcohol, ether, &c. have a bright green colour, a red fluorescence, and a well-known absorption spectrum. Nitrogen, according to the otherwise discordant analyses of both Gautier and Hansen, is present to the amount of 4—5 per cent. Iron, the author considers, is not an essential constituent.

In Dr. Schunck's opinion, the bands at the blue end of the absorption spectrum do not belong to chlorophyll, in his sense of the term.

The question is next raised whether chlorophyll is a homogeneous body or a mixture of several substances very similar in their properties? But, on this point, an absolute conclusion has not yet been reached. The decompositions of chlorophyll are then considered—that occurring on mere exposure to air and light, and that induced by the action of acids. Its behaviour with alkalies, which is very interesting, has been studied by Dr. Russell, F.R.S., and Mr. Lapraik. The most remarkable of the products obtained by the author is phyllotannin, concerning which Dr. Schunck remarks:—"There are few natural colouring-matters or derivatives which surpass phyllotannin and its derivatives with regard to beauty, combined with absorption spectra of singular elegance."

The action of aniline on chlorophyll is a new branch of enquiry which the author hopes to resume.

The occurrence of chlorophyll in the animal organism is admitted on the authority of Prof. Ray Lankester, of Dr. McMunn, and of Pocklington. Its function is probably respiratory. As regards its duties in plants he considers that the carbonic acid, which forms one of its constituents, "being held more loosely combined than in an ordinary carbonate, and yet in a state of greater condensation than it would be in a mere watery solution, would be in a favourable condition for transfer to the assimilating plasma which effects its decomposition with elimination of oxygen." The chlorophyll then takes up fresh quantities of CO_2, acting, therefore, as a carrier of carbonic acid in the plant, just as hæmoglobin conveys oxygen in the animal economy.

In this memoir, which is illustrated with figures of absorption spectra, Dr. Schunck has not merely given an excellent summary of our present knowledge of the chemistry of chlorophyll, but he has added some novel facts of value and has pointed out paths for further research. The physicist, the chemist, and the biologist will alike read his results with interest.

On the Pentane Standard and Pentane Lamps. By A. V Harcourt, M.A., F.R.S., with an Appendix by W. Stepney Rawson. Birmingham: J. Wright and Co.

Now photometry has become an operation of constantly recurring necessity, the question of a standard which shall be convenient, trustworthy, and shall always give comparable results has become one of grave importance. The standard source of light legally recognised in this country is the sperm candle of a fixed size and weight. But, unfortunately, however carefully they may be prepared the quantity of light which they give out is not absolutely uniform. Spermaceti itself is not a definite chemical individual, and in practice the manufacturer adds to it a small proportion of beeswax—four or five per cent. Hence, the melting-point of the sperm as used is not absolutely constant. There is no definition given by the Acts of the number and size of the threads of the wick, the closeness of the plaiting of the strands, and the degree of tightness to which the threads are stretched, though all these conditions affect the light of the candle. Series of tests made with different samples of candles, both coming within the parliamentary definition, gave results differing by five or six per cent. The methods of using them admit also of variations which affect the results.

Hence, an amended standard appears desirable, and such is accordingly proposed by Mr. Vernon Harcourt. He suggests a pentane lamp, otherwise known as an "air-gas flame," as a normal source of light. Full instructions are here given for the preparation and use of this mixture.

From the experiments here mentioned it appears that the results obtained with the air-gas flame are decidedly more constant than those with the normal candle. We read that Mr. W. G. Wood, one of the official gas examiners, was instructed in Mr. Harcourt's method, and on that and the following day made a series of testings of a stored coal-gas alternately with Mr. H. B. Dixon. Mr. Wood made eight readings of the illuminating power, the lowest being 16·6 and the highest 16·9. Mr. Dixon made eleven readings, of which the lowest was 16·6 and the highest 16·8. Their mean results differed by less than $\frac{1}{10}$ candle.

In view of such satisfactory results the propriety of adopting the pentane lamp in place of the standard candle ought to be taken into serious consideration.

Water-Works Statistics, 1889. Edited by Charles W. Hastings.

Gas-Works Statistics, 1889. Edited by Charles W. Hastings.

The Gas and Water Companies' Directory, 1889. London: Hazell, Watson, and Viney.

Of these three useful compilations the "Water-Works" is the least complete. Not, it would evidently appear, from any neglect on the part of the Editor, but from the disinclination of the officials to fill up the schedules of inquiry. Why they should be less communicative than the authorities of gas-works it is not easy to see. We still find no returns from Aylesbury, Tring, Kingston, and Salford. This is the more striking as the Chiltern Hills Company, who supply the two former towns, have no reason to be ashamed of the quality of the water which they furnish. On page 4 is the intimation that a certain water requires to be hardened—a very unusual complaint, except for dyeing-blacks. The "character" of the waters is often given very vaguely. Thus, one water supply calls itself "softer than chalk-water generally."

We do not see that any gas-work has, this year, achieved the feat of selling more gas than it has made, but one little town has sold exactly the quantity which it produced. In the illuminating power of gas Scotland still takes the lead. Many are given at 30-candle power, Tain at 32, Stow and Banchory at 33, and Colinsburgh (oil-gas) at 65! We see no mention of the production of water-gas, which is, we believe, already manufactured on the large scale, and which has a great future before it if the difficulty of the possible escape of carbon monoxide can be prevented.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 20, May 20, 1889.

On the Terrestrial Origin of the Oxygen Rays in the Solar Spectrum.—J. Janssen.—(See p. 281).

The Impossibility of Diamagnetic Bodies.—P. Duhem.—The author concludes that the existence of diamagnetic bodies is incompatible with the principles of

thermodynamics. To explain the existence of diamagnetic bodies in nature he reverts to the hypothesis of E. Becquerel, admitting that the supposed diamagnetic bodies are merely magnetic substances immersed in a medium more strongly magnetic.

The Variations of the Acid Function in Stannic Oxide.—Leo Vignon.—The author concludes that there exists an entire series of stannic acids, the first term of which is the soluble acid and the last is the ignited metastannic acid. These acids are formed by successive condensations, effected, not by the elimination of water, but by molecular transpositions coinciding with a gradual decrease in the intensity of the acid function.

On Oxalomolybdic Acid and the Oxalomolybdates.—A. Péchard. — Molybdic acid dissolves readily at a boiling heat in oxalic acid, yielding a syrupy liquid which crystallises on evaporation. The paper includes a description of the silver, barium, and sodium oxalomolybdates. Oxalomolybdic acid, if moist, turns blue on exposure to the sun's rays. Characters traced on paper with a solution of the acid on exposure to the sun quickly take an indigo-blue colour. This blue colour disappears on contact with water. If characters traced upon paper with the acid are very strongly heated they turn black, and are then no longer effaced by water.

On Phosphorous Acid. — L. Amat. — An aqueous solution of sodium pyrophosphite is converted into an acid phosphite the more rapidly as the solution is stronger and the temperature higher. The presence of an acid accelerates the transformation.

Action of the Alkaline Meta-, Pyro-, and Ortho-Arseniates upon the Alkaline Earthy Oxides.—M. Lefèvre.—In the researches it is found that calcium has a greater tendency to form chloro-arseniates than barium. On the other hand, barium has a greater tendency to form simple compounds than calcium, strontium taking an intermediate position.

On the Ammonium Malonates.—M. Massol.—A thermo-chemical paper, not admitting of useful abstraction.

The Proportion of Nitrates Contained in the Rain Water of Tropical Regions.—A. Müntz and V. Marcano.—One of the stations of observation selected by the authors is at Caracas (Venezuela), in 10° 3′ N. Lat., and at the elevation of 922 metres. The mean temperature is 21·8°, the rain-fall is irregular, and the storms severe and frequent. The observations extend over two years, and refer to 121 samples. The general mean of nitric acid was 2·23 m.grms. per litre. On one occasion it rose to 16·25 m.grms., and on another it was as low as 0·20 m.grms. On the contrary, at Liebfrauenberg, in Alsace, Boussingault found a mean of only 0·18 m.grm. nitric acid per litre, and at Rothamsted Messrs. Lawes and Gilbert obtained a mean of 0·42 m.grm. If we compare the total quantity of nitric acid thus brought down to the ground yearly, the difference appears still greater, as in tropical countries the annual depth of rain is generally greater than in temperate climates. At Caracas the rain-fall is about 1 metre. The quantity of nitrogen brought to the soil in the state of nitrate is 5·782 kilos. per hectare, whilst in Alsace it is only 0·330 kilo. and at Rothamsted 0·830 kilo. In the Island Reunion the mean nitric acid per litre of rain is 2·67 m.grms., or, taking the rain-fall at 1 metre, 6·93 kilos. of nitric nitrogen per hectare. In such climates the rain-fall alone supplies a nitrogenous manuring equal to about 50 kilos. of nitrate of soda yearly.

On the Richness of Wheat in Gluten.—E. Gatelier and L. L'Hote.—The authors conclude that the gross yield of grain and the proportion of gluten may be simultaneously increased by proper manuring and by the selection of suitable varieties.

The Alcoholic Fermentation of Milk.— M. Martinand.— Under certain conditions the alcoholic fermentation of milk, and its coagulation, may be effected with all kinds of yeast.

MISCELLANEOUS.

Pharmaceutical Society.—At a meeting of the Council of this Society on June 5th, Mr. Michael Carteighe was for the eighth time re-elected President. Mr. Alexander Bottle was re-elected Vice-President, and Mr. John Robbins Treasurer.

Action of the Alkaline and Earthy-Alkaline Metals upon the Animal Organisms.—A. Curci.—The author shows that rubidium and cæsium, like potassium, increase the pressure of the blood, and have the same characteristic action upon the pulse as potassium. Potassium, rubidium, and cæsium form a definite pharmacological group, all of which at first violently excite the muscular fibres of the blood-vessels, but in larger doses have a paralysing effect. Magnesium and calcium increase the pressure of the blood. Calcium, barium, and strontium have a peculiar effect upon the organs of circulation in cold-blooded animals. After the heart has come to a stop the striped muscles and the nervous system still act for a long time.

MEETINGS FOR THE WEEK.

Wednesday, 19th.—Meteorological, 7.
—— Geological, 8.
Thursday, 20th.—Royal, 4.30.
—— Chemical, 8. Ballot for the Election of Fellows.
Saturday, 22nd.—Physical, 3. "Researches on the Electrical Resistance of Bismuth," by Dr. Edmond Von Aubel.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 9606 of 1884 granted to William Weir Grieve for "Improvements in producing yellow colouring matter suitable for dyeing and printing."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed) H. READER LACK, Comptroller-General.

J. H. JOHNSON & CO.,
47, Lincoln's Inn Fields, London, W.C.,
Agents for The Farbenfabriken vormals Friedrich Bayer and Co.

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Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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NOTICE IS HEREBY GIVEN that The Farbenfabriken vormals Friedrich Bayer and Co., of Elberfeld, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 3803 of 1885 granted to Herbert John Haddan for "Colouring matters obtainable by the combination of tetrazo-ditolyl or tetrazo-dixylyl salts with alpha- and beta-naphthylamine or their mono- and disulpho-acids, and process for the manufacture of the same."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 5th June, 1889.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1543.

ON THE

OCCURRENCE OF SKATOLE IN THE VEGETABLE KINGDOM.*

By WYNDHAM R. DUNSTAN, M.A., F.C.S.,
Professor of Chemistry to and Director of the Research Laboratory of the Pharmaceutical Society of Great Britain.

Celtis reticulosa is the name of a large tree growing in Java, whose wood possesses an intolerable odour. A few pieces of this wood, when distilled with water, yielded a minute quantity of a solid crystalline substance having a fæcal odour, which, after purification, melted at 93·5° C. It afforded a crystalline picrate, by the analysis of which the substance is shown to possess the composition of methyl-indole (C_9H_9N), and is proved to be identical with the Pr3-methyl-indole or skatole which Brieger isolated in 1877 from human fæces, and Salkowski afterwards obtained from the putrefaction products of various kinds of animal proteid. Nencki has observed the formation of the same substance when potash is fused with albumen, and it has also been prepared synthetically. Skatole from *Celtis reticulosa* corresponds in all its properties with synthetical skatole from propylidene-phenyl-hydrazide.

The occurrence of skatole in a plant has not hitherto been observed.

Indole is associated with skatole in human fæces, but no indole could be detected in the wood of *Celtis reticulosa*.

ON THIOCAMF—A NEW DISINFECTANT MATERIAL.†

By J. EMERSON REYNOLDS, M.D., F.R.S.

Every practical physician is asked from time to time "How can I most easily disinfect that room?" after infectious illness or death has occurred in a household: and the answer is by no means simple. The difficulty is to recommend anything sufficiently easy of application in which confidence can be placed.

Chloride of lime, Condy's fluid, carbolic acid, &c., are all more or less good if they can be brought into direct contact with the things to be disinfected; but that is just the difficulty in the case of a room, for mere exposure of the above-named substances in solution or otherwise in a chamber is useless. If carefully *sprayed* they—especially carbolic acid—can do effective work; but thorough spraying involves the presence of the operator in the room, to his discomfort and possible danger, or the use of costly and troublesome apparatus.

It is evident then that apartments can only be disinfected in any real sense by gases or vapours of very volatile substances which are known to possess the requisite power of destroying the vitality of various bacteria. We are therefore practically reduced to chlorine gas, nitrous fumes, or sulphur dioxide gas; but all the common methods for the production of these in sufficient quantity are more or less dangerous, and disinfection by them can only be properly carried out by skilled persons, since there is risk of corrosion by powerful acids, or of setting fire to woodwork, &c.

Since writing the chapter on "Disinfection and Contagion," in the "Manual of Public Health," I have sought some simpler means than is there recommended for disinfection of rooms, so that any intelligent person could attain the end in view without risk of fire, without the use of corrosive materials, or of large quantities of any agents, and without involving the presence of the operator in the room, or the employment of special apparatus.

This search has been successful, and I have now the pleasure of bringing under your notice the singular liquid which fulfils the conditions I have just specified, and to which the name of Thiocamf has been given.

The basis of this novel disinfectant is a very curious liquid which results when sulphur dioxide gas is brought in contact with camphor. At ordinary temperatures the gas alone requires a pressure of more than two atmospheres to liquefy it; but camphor, owing to chemical attraction, can liquefy the sulphur dioxide gas without any pressure whatever. In this liquid are dissolved several known bactericides, therefore Thiocamf is *all* disinfectant; but I am not free to enter into further particulars, as the patent specification has not yet been published.

A quantity of the liquid has been preserved in my laboratory for nearly two years in a corked bottle, and has not undergone sensible alteration during that time.

Thiocamf possesses almost unique properties; for, while it can be preserved *without* pressure in bottles at mean temperature, mere exposure of the liquid in a thin layer to the air determines the steady evolution of relatively enormous volumes of sulphur dioxide gas from it, charged with the vapours of other powerful disinfectants. These gases and vapours diffuse through the whole of the air of a well-closed room, and therefore must reach everything in the room if given reasonable time.

The question then arises whether the sulphur dioxide gas can destroy the bacteria—particularly the infective forms—when it reaches them. The evidence on this point has hitherto been of a rather loose kind, though the results led to the conclusion that sulphur dioxide gas is a powerful bactericide. Happily the truth of this conclusion has now been placed beyond doubt by a critical investigation of the subject, aided by modern methods of bacteriological study. This examination has been carried out in Paris by MM. Dubief and Bruhl, under the direction of Dr. Dujardin-Baumetz, and the results have been recently communicated to the Academy of Sciences. (*Comptes Rendus*, cviii., 324).

Starting with air rich in germs of various kinds, and combining Miquel's method of numbering the bacteria with alkaline culture, Dubief and Bruhl found that the germs were always reduced in number after the action of diluted sulphur dioxide gas; therefore the latter destroyed the vitality of bacteria. It was further found that the number destroyed increased with the duration of the action of the gas, and that this destructive action was accelerated when the humidity of the air was increased.

In all the experiments with the rather dilute sulphur dioxide gas used the *latter proved particularly fatal to micrococci* and allied bacteria, whether diffused through the air of a chamber or attached to its walls. As these are organisms of the class which true disinfectants seek to destroy, this testimony to the value of sulphur dioxide is of exceptional importance.

Lastly, those investigations have shown that sulphur dioxide gas is a true bactericide even in a dry state, though longer time is then required for the production of its full effect,

The bearing of these results on the value of Thiocamf is obvious, for if simple sulphur dioxide gas be the powerful bactericide MM. Dubief and Bruhl have proved, the mixture of sulphur dioxide with vapours of other disinfectants of acknowledged value should be a reliable combination. Moreover, there is no material that I know of, save Thiocamf, which can give off so large a relative volume of sulphur dioxide gas (the contents of a small six ounce bottle can afford over 20,000 c.c.) without any special treatment, save exposure in a very thin layer on

* Abstract of a Paper read before the Royal Society, June 6, 1889.
† Read before the Royal Dublin Society, May 22nd, 1889.

an old tray or dish to the air of a room to be disinfected. Further, one ounce of Thiocamf shaken up with a quart of water forms a powerful disinfectant for ordinary purposes, such as sprinkling over various matters, purifying drains, &c.; while a still more dilute solution (one ounce to a gallon) can be used for soaking clothes which have been in contact with infected persons. The residue of Thiocamf has a pleasant aromatic odour.

This concentrated disinfectant can now be obtained at a cheap rate, as a company formed for its manufacture, can produce several hundredweight of Thiocamf per week.

NOTES ON BURMESE PETROLEUM.

By the late R. ROMANIS, D.Sc., Rangoon College.

THE petroleum wells of Burma are found in two great groups: the Irrawaddy Valley, eastward of the Arracan Yoma, and the Kyauk-Pyn and Borongas group to the westward. The first, or Irrawaddy group, seems to be the longest known, having been worked for at least two centuries. It includes four districts, Yay-nan-chaung, Pagan, Yaw, and Mimbu. The first of these, Yay-nan-chaung, is the centre of the Burmese petroleum industry; at Pagan there is a group of a few wells worked in an indolent fashion; in the Yaw and Mimbu districts there are a few surface springs of petroleum, but no wells—in fact, the Yaw district is not yet opened up by roads, and is hardly known.

The petroleum from Yay-nan-chaung and Pagan is generally a viscous liquid of sp. gr. from 0·850 to 0·900, with a strong green fluorescence, solidifying about 24° C.; but curious variations have been observed even in closely adjacent wells.

The method of working is described in Yule's "Ava" and elsewhere. Shortly, it consists in sinking a well about 4 feet square, roughly lined with timber, through the strata of soft sandstone, shale, and limestone until the gas issuing from the sand stops further progress, generally at a depth of 300 feet, in a bed of shale with thin layers of sand.

The flashing-point of the fresh oil is about 3° or 4° above the melting-point, but, by the time it reaches Rangoon in the oil barges, the flashing-point rises to 35°, or even higher, by evaporation of the volatile portion. It contains a notable proportion of benzene, and 11 per cent of solid paraffin. When refined at Rangoon it yields about 30 per cent of burning-oil (flashing-point = 36), about the same quantity of lubricating and batching oil, and 5 per cent of solid paraffin. It was this substance that was examined by De la Rue and Miller, under the name of Rangoon tar (*Proc. Roy. Soc.*, viii., 21). Their specimen, no doubt, had lost the volatile part by exposure to the air during the long voyage down the Irrawaddy to Rangoon in earthern pots on board native boats. As now obtained, by American drills, from a greater depth than the natives could reach, and brought rapidly to Rangoon in tank barges, it generally contains gas in solution as well as benzene.

The only well in the Irrawaddy Valley, in the province of Lower Burma, at Padoukben, near Thayetmyo, produces petroleum of the same kind as Yay-nan-chaung.

To the westward of the mountains in the province of Arracan a different kind of oil is found. Arracan oil, whether from the Borongas or from Kyauk-Pyn, is a reddish brown limpid liquid, sp. gr. at 32° C. 0·825. It does not solidify. The flashing-point is 40° C. by Abel's test, and it, like the Yay-nan-chaung oil, contains much benzene and hydrocarbons of the aromatic series.

There are two groups of oil wells in Arracan, one in the Borongas islands, and the other near Kyauk-Pyn. A company was floated to work them by American methods, but resulted in failure from some cause or other, although the crude oil yields over 70 per cent of burning oil. There is some trade done by natives yet in this oil, which is used throughout Arracan for burning in lamps, being preferred to all others by the Arracanese.

The following is the result of the fractional distillation of a specimen from an unknown locality in Arracan; I believe from Kyaukpyn:—

Gas was evolved at 30° C. Liquid began to distil at 70° C.

70— 90°	3·1 per cent
90—100°	7·6 ,,
100—130°	10·6 ,,
130—200°	18·7 ,,
200—300°	18·7 ,,
Over 300°	12·5 ,,
Heavy oil left in retort	8·0 ,,
Paraffin crystals	3·1 ,,
	82·3 ,,
Loss..	17·7 ,,

The same distilled in a current of steam at—

100°	23·3 per cent
100—110°	33·0 ,,
110—130°	29·3 ,,
Residue	13·3 = heavy oil.

The strata in which this petroleum is found are much disturbed and full of faults; adjacent wells give very different results; and generally they soon run dry. At Yay-nan-chaung, although the geological features are similar, yet the duration of the wells seems much greater. The present out-turn at Yay-nan-chaung is about 15,000 tons per annum, but could be easily increased if there were a demand for it.

FURTHER NOTES ON THE VOLUMETRIC ESTIMATION OF NICKEL, WITH A NEW METHOD FOR ITS APPLICATION IN PRESENCE OF IRON, &c.

By THOMAS MOORE.

ON a previous occasion I gave a description of a method for the volumetric estimation of nickel, by means of which a rapid and tolerably accurate determination of that metal may be arrived at. In following up the experiments it has been found that large quantities of ammonic salts, or the presence of manganese, interferes with the accuracy of the process. The presence of the former may be got rid of by employing the basic acetate method for the iron-nickel separation, instead of repeated precipitation by ammonic hydrate, and titrating the filtrate after the addition of a small quantity of ammonic hydrate with potassic cyanide, and certainly the results so obtained are sufficiently accurate for all practical purposes; nevertheless, there is still the unpleasant fact that the basic precipitation must be repeated at least three times, giving a large filtrate which requires some hours for its concentration before being reduced to a convenient volume, besides containing all the manganese, and, very often, some aluminium. Bearing these difficulties in mind, I endeavoured to find a process by which the presence of these foreign bodies would be rendered immaterial, or, at least, innocuous, with the result that iron, aluminium, zinc, and small quantities of manganese have no deleterious action whatever, and, furthermore, their preliminary separation is rendered quite unnecessary. This object is attained by adding to the slightly acid solution an excess of sodic pyro-phosphate until the precipitate which first formed is re-dissolved, and forms, even in presence of much iron, a practically clear colourless solution; this is then *slightly* acidified with hydrochloric acid, thereafter rendered distinctly alkaline with

ammonic hydrate. To this solution the standard potassic cyanide (22 to 25 grms. KCN per litre) is added until the blue colour disappears; now add a measured quantity of cupric ferrocyanide emulsion, and continue the addition of the cyanide until the violet-brown colour is replaced by yellow, the formation of which is most distinctly seen when the titration takes place in an evaporating basin. It will be at once noticed that a great advantage gained by this process is that the necessity for the separation of iron, &c., is done away with. In those cases where zinc is present, the potassic cyanide must be added slowly, and only until the colour of the cupric ferrocyanide disappears, as in this case if titrated until the yellow appears, the results are too high.

In place of an emulsion of cupric ferrocyanide, a solution of the same in ammonic oxalate may be employed, thus dispensing with the necessity of agitating previous to use, and rendering it more uniform.

Subjoined I give a few of the results obtained by this process, compared with those obtained by the usual methods for electro-deposition, which amply testify to its accuracy and utility.

	Electro-deposition. P.c. Ni.	Volumetric. P.c. Ni.
Mineral 1 (containing Ni, Fe, Mg, Al)	6·65	6·62
„ 2 „ „	7·00	7·05
„ 3 „ „	12·45	12·45
„ 4 „ „	13·98	14·04
German silver „ „	11·25	11·31
„	18·66	18·69

Thio, New Caledonia.

DETERMINATION OF NITRIC NITROGEN BY MEANS OF FERROUS SULPHATE.

By M. BAILHACHE.

Pelouze first applied the reaction of nitric acid with the ferrous salts for the determination of nitrates, making use of ferrous chlorides. This method is defective; Fresenius declared the results variable, and enumerated the chief causes of their want of accuracy. In consequence, all the agricultural stations have adopted the method of Schlœsing with Grandeau's modification. This method has been applied for a long time by the author at the Agricultural Laboratory of Seine-et-Oise. Its tediousness and the frequency of absorptions compelled him to seek for a method equally accurate and more expeditious. Such a method he considers that he has found in a modification of the process of Pelouze. Instead of the chloride he uses ferrous sulphate strongly acidulated with sulphuric acid. He thus avoids the losses of iron by volatilisation against the heated sides of the flask, which often happens when the chloride is used. Further, as the sulphuric solution of ferrous sulphate boils at a higher temperature, the whole of the nitric oxide is more rapidly expelled.

The apparatus consists of a flask marked at 250 c.c., to which is fitted a caoutchouc stopper traversed by two tubes. One of these is from 5 to 6 c.m., and is drawn out at its upper end. The second tube descends to half a c.m. from the bottom of the flask. It is surmounted with a funnel fitted with a tap, having a cylindrical form and a capacity of 35—40 c.c. This funnel serves not only for the introduction of the nitrate to be examined, but also for the gentle influx at the beginning and the end of the operation of a solution of sodium hydrocarbonate, the carbonic acid of which, at the outset, expels the air of the apparatus, and at the end drives out the last traces of nitric oxide.

For titrating the residue of iron not peroxidised, the author uses potassium dichromate, potassium ferricyanide serving as indicator.

The following solutions are needed :—Ferrous sulphate containing per litre 100 grm. actual sulphate, and 75 c.c. of monohydrated sulphuric acid; potassium bichromate containing per litre 17·85 grms. of the pure dry salt; a solution of sodium nitrate containing 50 grms. of the pure dry salt per litre; and a solution of sodium hydrocarbonate saturated in the cold. The chromic solution peroxidises exactly its own volume of the ferrous solution, and both correspond to 10·192 grms. sodium nitrate per litre.

To carry out the process there are introduced into the flask 50 c.c. of the ferrous sulphate solution and 25 c.c. of monohydrated sulphuric acid. The flask is shaken up, and the stopper, with its two tubes, is inserted. The flask is then set on a sand-bath capable, if needful, of holding five or six such flasks. The tap is shut and 25 c.c. of the sodium hydrocarbonate solution are placed in the funnel. The tap is then regulated so that this liquid may flow in drop by drop. The liquid boils, and the ebullition continues as the funnel empties. Before all the liquid has run off there are introduced into the funnel 10 c.c. of the standard solution of sodium nitrate.

At this moment the operator concentrates his attention on the continuity of the ebullition and the regular escape of the nitric oxide, which ought never to become tumultuous and never to stop.

As the liquid escapes from the funnel the contents of the flask become more and more deeply brown. The tap is closed before the funnel is completely empty. When the deep brown colour of the liquid has disappeared, 25 more c.c. of the solution of hydrocarbonate are introduced into the funnel and let flow gently into the flask; the tap is closed and the fire withdrawn. It is then let cool, the volume is made up with distilled water, the flask is shaken, and the residual iron not peroxidised is titrated with the chromic solution.—*Comptes Rendus*, Vol. clviii., No. 21.

OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT.*

By EDGAR F. SMITH.

In using the electric current for the determination and separation of metals, it occurred to me that its oxidising power might be utilised to convert sulphur and other elements into higher oxides, thus bringing them into forms in which they could be readily determined. To test this I undertook the oxidation of the sulphur in chalcopyrite after the following manner: About ten grms. of solid potassium hydroxide were placed in a small nickel crucible, and carefully heated over a Bunsen burner until the water was expelled, when the flame was reduced, so that its heat was just sufficient to retain the alkali in liquid form. The crucible was put in connection with the positive pole of a battery, and the powdered mineral placed upon the alkali. A heavy platinum wire, from the negative pole, extended just under the surface of the fused mass, and, when the current was passed, a lively action ensued, accompanied with considerable spattering. Loss was prevented by placing a perforated watch-crystal over the crucible. When the action had continued for ten minutes the connection was broken, the crucible and its contents allowed to cool, placed in a beaker, covered with water, and warmed upon an iron plate. On filtering off the insoluble oxides the filtrate was blue in colour, due to a little copper. The liquid was acidulated with hydrochloric acid, and care taken to detect any hydrogen sulphide or sulphur dioxide, which are always present, when the oxidation of the sulphur is incomplete. In this particular case all the sulphur was changed to sulphuric acid and removed as barium sulphate. When ignited the

* Chemical Section of the *Journal of the Franklin Institute*, April, 1889.

latter presented a perfectly white appearance, showing not the slightest trace of iron.

Having succeeded so well with the first portion I weighed off 0·1734 grm. chalcopyrite, subjected it to a like treatment, and obtained 0·4086 grm. $BaSO_4$=0·0561 grm. S or 32·35 per cent S. One of my students oxidised another portion (0·5 grm.) of the same material with nitric acid and potassium chlorate and obtained 32·54 per cent sulphur.

The current used above registered one ampère (10·45 c.c. HO gas) per minute as it passed through the fused alkali. The solution containing the potassium sulphate contained no iron. A little copper was present in it. The residue of oxides (Fe_2O_3, CuO, &c.) should dissolve readily and completely in warm hydrochloric acid. There may, however, be a residual mass, red in colour, but this can be disregarded, as it is only metallic copper. In some of the oxidations the wire attached to the negative pole was coated red by copper, or with a black deposit of metallic iron. The idea suggested itself to me that, as the metal was depositing as such, it might possibly inclose some mineral, as yet unacted upon, and thus withdraw it from the field of oxidation. I therefore invariably, in every determination, reversed the current for a few minutes before its final interruption. This seems to have been unnecessary with chalcopyrite, but was required with some other minerals with which similar experiments were tried.

With a chalcopyrite different from that analysed before the following percentages of sulphur were obtained :—

(1) 29·9 p.c. S—(2) 30·11 p.c. S—(3) 29·7 p.c. S.

The quantity of mineral used was in (1) 0·1528 grm., in (2) 0·1445 grm., and in (3) 0·1082 grm. About 10 grms. of potassium hydroxide were used in each determination. The current was one ampère, acting for a period of ten minutes. In working with a quantity of mineral varying from 0·2 — 0·3 grm. the quantity of alkali should be doubled.

This method affords a rapid oxidation of sulphur to sulphuric acid, so that the inconveniences arising from the slow time-consuming method with nitric acid and potassium chlorate, or that with nitric acid alone, can be avoided, where a current of the strength indicated above can be obtained.

Iron salts also are removed. I have endeavoured to oxidise the sulphur of pyrite by this means, but thus far the experiments have been fruitless. I have not obtained more than half of the sulphur in the form of sulphate. Even when the current acted for thirty minutes the result was no better. The cause of this singular behaviour appears to be due to the presence of the iron. I expect, however, to so modify the experiment in this case that pyrite may yet be as easily oxidised as chalcopyrite.

As time permits this mode of oxidation will be extended to other natural sulphides and to compounds containing sulphur.

My experiments in oxidising with the current really began with chromite. It was treated the same as the chalcopyrite. Twice I obtained a little over fifty-three per cent Cr_2O_3 from a specimen of this mineral, which, by an older method, gave fifty-four per cent Cr_2O_3. At present I am not prepared to say anything more in regard to this mineral. Some difficulties have appeared which require solution before entering into details.

Nickel crucibles, as well as iron, have been used in this work, and with chromite an old platinum vessel was made to do service. The crucibles were one and one-fourth inches in height, and one and three-eighths inches wide; the most convenient form would be that measuring two inches in length and one and one-half inches in width.

In closing I must extend my sincere thanks to Mr. D. L. Wallace, of this laboratory, for his kind assistance, without which it would have been impossible for me to carry out these experiments at this time.

University of Pennsylvania, Philadelphia.

A PLATINIFEROUS NICKEL ORE FROM CANADA.

By F. W. CLARKE and CHARLES CATLETT.

During the autumn of 1888 we received through two different channels, samples of nickel ores taken from the mines of the Canadian Copper Co., at Sudbury, Ont. From one source we obtained two masses of sulphides, to be examined for nickel and copper; from the other source came similar sulphides, together with a series of soil and gravel-like material, seven samples in all. In the latter case an examination for platinum was requested, and in five of the samples it was found, the gravel above mentioned yielding 74·85 ozs. of metals of the platinum group to the ton of 2000 lbs. At the outset of the investigation we were decidedly incredulous as to the existence of platinum in such ores; but the discovery of sperrylite by Mr. Wells in material from the same mines gave our work a wholesome stimulus, and the assays were carefully carried through.

The sulphide ores submitted to us from Sudbury were all of similar character. They consisted of mixed masses, in which a grey readily tarnishing substance was predominant, with some chalcopyrite, possibly some pyrite, and a very little quartz. Two samples were examined in mass; one gave 31·41 per cent of nickel with a little copper, the other gave 35·39 per cent of nickel, and 5·20 of copper. The nickel mineral itself proved to be a sulphide of nickel and iron, and as ores of that composition are not common, it was thought desirable to examine the substance further.

As above stated, the nickel mineral is the predominating constituent of the masses submitted for examination. It is steel-grey, massive, and exceedingly alterable in the air, and its specific gravity, determined by picnometer, is 4·541. An analysis of carefully selected material gave the following results :—

Ni	41·96
Fe	15·57
SiO_2	1·02
Cu	0·62
S	40·80
	99·97

Neither cobalt nor arsenic could be detected.

The foregoing figures work out sharply into the ratio R : S :: 4 : 5; and approximately into the formula Ni_3FeS_5. If we deduct silica, together with the copper reckoned as admixed chalcopyrite, and re-calculate the remainder of the analysis to one hundred per cent we have the following figures :—

	As found	Calc. as Ni_3FeS_5.
Ni	43·18	44·6
Fe	15·47	14·4
S	41·35	41·0
	100·00	100·0

In short, the mineral has the composition Ni_4S_5, with *about* one-fourth of the nickel replaced by iron. The only known species with which this agrees is Laspeyres's polydymite, of which the Sudbury mineral is evidently a ferriferous variety. What relations it may bear toward beyrichite, pyrrhotite, &c., is as yet a matter of considerable uncertainty. Probably in most cases the niccoliferous constituent of pyrrhotite is millerite, but other sulphides, like the polydymite, may perhaps occur also.

The polydymite which was selected for the above analysis came from the mass in which, in average, 35·39 Ni and 5·20 Cu had previously been found. The mass weighed several kilogrms., and was remarkably free from quartz. The same mass, with two smaller pieces

resembling it, were also examined for platinum, by the following method:—One assay ton of the finely ground ore was treated with nitric acid until all or practically all of the sulphides had been dissolved. The dried residue was then assayed in the usual manner; except that, to facilitate cupellation, a little pure silver was introduced into the lead button. From the final bead the silver was dissolved out by sulphuric acid, leaving the platinum in a finely-divided grey powder. The latter dissolved easily in aqua regia, and gave all the reactions needful to identify it thoroughly. The results were as follows, "A" representing the large mass in which the polydymite was determined.

A	2·55 ozs. Pt to the ton,	or	0·0087 per cent
B	1·8 „	„	0·0060 „
C	7·0 „	„	0·024 „

That the metal weighed was nearly all platinum is certain; but it may have contained small amounts of other metals of the same group. The material separated was not sufficient to warrant a search for the rarer associates of platinum. Probably the platinum exists in the ore as sperrylite, although this point was not proved. The amount of platinum in the mass most thoroughly examined would require to form sperrylite only about 0·007 per cent of arsenic, which is too small a quantity for detection by ordinary analysis. That platinum should exist in appreciable quantities in an ore of such character is something quite extraordinary. Whether it could be profitably extracted is an open question.—*American Journal of Science*, Vol. xxxvii., May, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Professor Mendeleeff's Faraday lecture on the Periodic Law of the Chemical Elements, owing to the enforced absence of the lecturer, was read by the Secretary.

At the conclusion of the lecture, a vote of thanks to Professor Mendeleeff was moved by Professor Frankland and seconded by Sir F. A. Abel.

The Faraday medal was then presented by the President to Mr. Anderson, by whom it was received on behalf of Professor Mendeleeff.

June 6th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. Alfred Edward Sibson, M. Carleton Williams, C. W. Priestley, A. L. Stern, T. E. J. Cridland, and B. Brauner were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Thornton Addyman, Queenwood College, Hants; Charles Frederick Baker, B.Sc., 27, London Road, N.W.; John Simpson Ford, 11, Abbotsford Park, Edinburgh; J. T. Norman, 2, Mornington Road, Regent's Park, N.W.; Sydney Steel, Fairlawn, Blackheath; John Bishop Tingle, Jäger Strasse, F/iv., Munich.

The President drew attention to the large number of interesting papers to be brought before the Society that evening, and expressed the hope that the authors present would endeavour to give an account of the essentially important points in their communications without entering into details which could not be appreciated by listeners. He was of opinion that communications made at the meetings should almost invariably be of a different character to the published papers, and should be divested of details; and he ventured to express the hope that authors generally would accept this suggestion.

The following papers were read:—

52. "*Experimental Researches on the Periodic Law.* Part I., *Tellurium.*" By B. Brauner, Ph.D.

The author gives a detailed account of his attempts to determine the atomic weight of tellurium by as many different methods as possible; in all 11 were adopted, but each gave a different result, varying from 125—140. He eventually succeeded, but with great difficulty, in preparing what appeared to be pure tellurium tetrabromide, and on most carefully analysing this obtained the value Te=127·64 (O=16). This number, however, is incompatible with the position of tellurium in the periodic system, and having satisfied himself that there were no experimental errors which could account for the discrepancy, the author was forced to conclude that what had hitherto been regarded as pure tellurium contained foreign elements. By submitting tellurium solutions to a systematic fractional precipitation, he has, in fact, succeeded in obtaining a variety of substances, some of which are undoubtedly novel elements. One of these it is proposed to call *Austriacum* (*Austrium*). In all probability this is the *Dvi-tellurium* (212), the probable existence of which was pointed out for the first time by Mendeleeff in his recent Faraday lecture. From analyses made with material, the uniformity of which is not yet quite established, the author is satisfied that the atomic weight of the element in question approaches very closely to that indicated by Mendeleeff. In addition, there is at least one other novel constituent, and this appears to be more or less closely allied to arsenic and antimony. It follows that true tellurium has yet to be discovered, and that its atomic weight and properties remain to be determined.

Discussion.

Mr. J. Newlands remarked that he had always placed tellurium below iodine; he had no doubt that the exceptional atomic weight would ultimately be rectified, and that true tellurium, when isolated, would be found to have an atomic weight near 125.

53. "*The Amylodextrin of W. Nägeli and its Relation to Soluble Starch.*" By Horace T. Brown and G. Harris Morris, Ph.D.

Amylodextrin, described by W. Nägeli in 1874, is prepared by the long-continued action of cold dilute acids on intact starch-granules; when purified by dissolution in water and precipitation with alcohol, it forms crystalline spherules, closely resembling the well-known spherules of inulin. Amylodextrin is coloured a reddish brown by iodine. The values obtained on analysis of the purified substance were—

$[\alpha]j$ ..	3·86	206·25°	κ ..	3·86	9·07°

which correspond to a percentage composition of—

Maltose ..	14·87	which	$[\alpha]j$ ..	3·86	205·4°
Dextrin ..	85·13	requires	κ	3·86	9·07
	100·00				

The substance is shown to be a definite compound: (*a*) by its absolute unfermentability by ordinary top fermentation yeast; (*b*) by the impossibility of differentiating it by fractional precipitation or partial dissolution; (*c*) by its passing through a dialyser in an unaltered form; and (*d*) by its distinct crystalline form.

The authors consider amylodextrin to be analogous in composition to the malto-dextrin previously described by them (*Trans.* xlvii., 528), and assign to it the formula $C_{12}H_{22}O_{11}\cdot(C_{12}H_{20}O_{10})_6$; *i.e.*, it may be regarded as constituted of one *amylon* or maltose group in combination with six *amylin* or dextrin groups.

A determination of the molecular weight by Raoult's method gave the following numbers :—

	Calculated for $\{C_{12}H_{22}O_{11} \atop (C_{12}H_{20}O_{10})_6$.	Found (mean).
A	0·0096	0·0086
M	1962·0	2220·0

Amylodextrin, like malto-dextrin, is rapidly and completely converted into *maltose* by the action of diastase.

The authors point out that amylodextrin has been confused by former workers with soluble starch on the one hand, and with the so-called starch-cellulose on the other hand. From these substances it is differentiated by its solubility, its iodine colouration, and its behaviour with diastase and with acids. When acted on by diastase, soluble starch yields a mixture of maltose and dextrin corresponding to the No. 8 equation of the authors' previous papers, whilst amylodextrin is completely converted into maltose by the same treatment. The authors also show that soluble starch is the first product of the action of cold dilute acids on starch, and that this is slowly hydrolysed to amylodextrin, a portion of the starch substance at the same time going into solution as dextrose.

54. "*The Determination of the Molecular Weights of the Carbohydrates.*" Part II. By Horace T. Brown and G. Harris Morris, Ph.D.

After referring to their former paper on this subject (*Trans.*, 1888, 610), and stating that the results there given have been since confirmed by Tollens and Mayer (*Ber.*, 1888, 1566, and 3508), and by de Vries (*Compt. Rend.*, cvi., 751), the authors give the results of the determination by Raoult's method of the molecular weights of the following carbohydrates :—

Galactose.

	Calculated for $C_6H_{12}O_6$.	Found (mean).
A	0·106	0·1073
M	180·0	177·0

Inulin.

	Calculated for $2(C_{36}H_{62}O_{31})$	Found (mean).
A	0·0096	0·0087
M	1980·0	2176·0

Kiliani has assigned the formula $C_{36}H_{62}O_{31}$ to inulin, but the authors' results point to the correct value being double this. They have already shown the great similarity between amylodextrin and inulin as regards their physical properties (see preceding Abstract), and they are inclined to regard the two substances as closely analogous in composition, thus :—

$\{(C_{12}H_{22}O_{11})_2 \atop (C_{12}H_{20}O_{10})_4$; Inulin; M = 1980.

$\{C_{12}H_{22}O_{11} \atop (C_{12}H_{20}O_{10})_6$; Amylodextrin; M = 2286.

although the amylin and amylon groups in each possess very different optical and other properties, and the products of hydrolysis with dilute acid are very different.

Malto-dextrin.

	Calculated for $\{C_{12}H_{22}O_{11} \atop (C_{12}H_{20}O_{10})_5$.	Found (mean).
A	0·0191	0·0197
M	990·0	965·0

Starch.— It was found impossible to apply Raoult's method to starch-paste; solutions of soluble starch produced so slight a depression that no reliable results could be obtained: a number of fairly concordant results, however, pointed to a molecular weight of 20,000 to 30,000. In order to ascertain whether the failure in this case was due to a high molecular weight, and not to the fact that the method was inapplicable to colloid substances, an arabinic acid, having a rotatory $[\alpha]_j = +61·16°$, was examined; this gave A = 0·0265, M = 717·0, thus rendering it probable that the small influence exercised by soluble starch was due to its high molecular weight.

Indirect evidence was then sought for by an examination of the dextrins. The authors have previously shown that when starch is broken down by diastase, a resting stage in the reaction is reached when the amount of dextrin produced corresponds to *one-fifth* by weight of the starch taken, and that *the molecule of this stable dextrin is one-fifth of the size of the starch-molecule from which it has been derived.* Determinations made with several specimens of this low dextrin gave the following mean values :—

	Mean values.	Calculated for. $20C_{12}H_{20}O_{10}$.
A..	0·0030	0·0029
M	6221·0	6480·0

and consequently the formula of soluble starch would be $5(C_{12}H_{20}O_{10})_{20}$, and its molecular weight 32,400. The endeavour was also made to apply Raoult's method to the determination of the question whether the dextrins are a series of polymers, or whether they are simply metameric. For this purpose a number of the higher dextrins were prepared from starch-transformations which had been stopped at an early stage of hydrolysis. All the numbers obtained show that the freezing method affords no evidence of there being any difference in molecular weight between the high and low dextrins, the numbers being, in fact, almost identical.

From a consideration of the results obtained with soluble starch and with dextrins of varying position in the series, the authors conclude that the evidence points to the conclusion that the dextrins are metameric and not polymeric compounds. They therefore abandon their former working hypothesis of the hydrolysis of starch, and now suppose the starch-molecule to consist of four complex amylin-groups, arranged round a fifth similar group, constituting a molecular nucleus. When hydrolysis takes place this complex is broken up, four amylin-groups being liberated, which in turn are capable of undergoing complete hydrolysis into malto-dextrins, and ultimately into maltose, whilst the fifth amylin group which constituted the nucleus of the original molecule, resists the action of hydrolysing agents and forms the stable dextrin of the No. 8 equation.

Each amylin group of the five has the formula—

$$(C_{12}H_{20}O_{10})_{20},$$

corresponding to a molecular weight of 6480; the molecule of soluble starch being represented by $5(C_{12}H_{20}O_{10})_{20}$, corresponding to a molecular weight of 32,400.

Discussion.

Dr. Gladstone remarked that the observations made by Mr. Hibbert and himself on the molecular weights of colloid substances completely confirmed those now brought forward by the authors. He believed Raoult's method to be capable of distinguishing polymers, as satisfactory results had been obtained on examining polymeric C_5H_8 compounds.

Dr. Armstrong remarked that as both the universal applicability of Raoult's method and the molecular weights of colloids were in question, neither was at present a safe standard. He was not satisfied with the conclusion arrived at in the case of the dextrins.

55. "*Researches on Silicon Compounds. Part V.*" By J. Emerson Reynolds.

The author has already shown that silicon tetrabromide unites with some amidic compounds, especially thiocarbamide, allyl-, phenyl-, and diphenyl-thiocarbamides, without loss of halogen, and produces compounds of the type $(CSN_2H_4)_8SiBr_4$. In this part a detailed account is given of the products of interaction of silicon haloids with excess of aniline, orthotoluidine, and paratoluidine, and the three following bodies are described which result

from the complete substitution of halogen by NHR-groups derived from the amido-compounds.

Silicotetraphenylamide, $Si(NHC_6H_5)_4$, a beautiful crystalline body, is obtained from its carbon disulphide solution in fine monoclinic forms which have been subjected to a determined crystallographic examination by Professor Sollas.

Silicoparatolylamide, $Si(pNHC_7H_7)_4$, is obtained from its benzene solution in botryoidal masses of fine needles; it is but slightly soluble in ligroin, and therefore is precipitated by it from a benzene solution.

Silico-orthotolylamide, $Si(oNHC_7H_7)_4$. This differs from the para-compound in being soluble in ligroin. When the mixed benzene and ligroin solution is distilled a very thick syrupy liquid remains which, after long exposure in a vacuum, gradually affords a quantity of minute needles which do not exhibit any tendency to form aggregations.

56. "*The Isomerism of the Alkyl-derivatives of mixed Diazoamido-compounds.*" By R. Meldola, F.R.S., and F. W. Streatfeild.

The authors first describe a detailed series of experiments undertaken with the object of testing the chemical individuality of the mixed diazoamide—

$$(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m),$$

and its alkyl-derivatives. A critical study of the compound has served to confirm the former result that this compound and its alkyl-derivatives are perfectly definite, and that they cannot be formed by crystallising together the corresponding symmetrical compounds. Mixtures of $(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(p)$ and—

$$(m)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m)$$

can be easily separated into their constituents by crystallisation from alcohol. The same holds good for the corresponding ethyl-derivatives, which are equally capable of being separated whether formed separately and afterwards mixed or whether a mixture of the unalkylated compounds is first prepared and then afterwards ethylated by the authors' method. A more extended study of the mixed diazoamides containing a halogenised radicle has served to convince the authors that the mixed diazoamides are most difficult to prepare in a state of purity, owing to the tendency to the formation of the corresponding normal (symmetrical) compounds at the same time. It is pointed out as a result of this experience that all the mixed diazoamides prepared by Continental investigators have been of very doubtful purity, and that in nearly all cases a nitrogen determination only has been considered sufficient to establish the composition. It is shown that the presence of one or the other of the normal compounds might thus escape detection, as a considerable percentage of such an impurity would not affect the percentage of nitrogen beyond the ordinary limits of experimental error. Criticising their own former work in the light of this experience, the authors have come to the conclusion that the diazoamides from para- and meta-nitraniline are not so well adapted for ascertaining when a pure product is obtained as those mixed compounds which form the subject of the present paper, and which contain a halogenised radicle on one side of the N_3H-group. The mixed compound derived from the two nitranilines might obviously contain some of the dipara- or dimeta-compound without affecting the analytical numbers, since both sides of the N_3H-group have the same composition. Many new preparations have, therefore, been made and studied, and the melting-points revised with the following results:—

$(p)NO_2\cdot C_6H_4\cdot N_3H\cdot C_6H_4\cdot NO_2(m)$ .. 212—213° (instead of 211).

$(p)NO_2\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$ 151—155° (instead of 148).

This vagueness of melting-point has been found to be a very general character of all the alkyl-derivatives of mixed diazoamides prepared by direct alkylation, and is attributed to the circumstance that the melting-point is also the point of decomposition, this instability being especially observable in the case of the compounds containing strongly acid radicles. The authors re-state their original proposition, viz., that every pair of amines, $X\cdot NH_2$ and $Y\cdot NH_2$, can give rise to *three* isomeric alkyl-derivatives:—

1. By the action of diazotised $X\cdot NH_2$ on $Y\cdot NHR'$.
2. By the action of diazotised $Y\cdot NH_2$ on $X\cdot NHR'$.
3. By the direct alkylation of $X\cdot N_3H\cdot Y$.

A large number of triplets have been prepared, all of which conform to this proposition. Their formulæ and melting-points are:—

I.	$(p)NO_2\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	151—151·5°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2(p)$	163—164°
	$(p)NO_2\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Br(p)$ ..	150·5—151·5°
II.	$(p)NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot Br(p)$	139—140°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot NO_2(p)$	124—125
	$(p)NO_2\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot Br(p)$..	115—116
III.	$(m)NO_2\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	144°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot NO_2(m)$	160·5—161°
	$(p)Br\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot NO_2(m)$ ..	125—137·5 (much decomposition
IV.	$(m)NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot Br(p)$	111°
	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$	135—136°
	$(p)Br\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot NO_2(m)$..	96—117 (much decomposition
V.	$(p)Br\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot CH_3(p)$	113—114°
	$(p)CH_3\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$	99—99·5°
	$(p)CH_3\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Br(p)$ ..	97—97·5
VI.	$(p)Cl\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot CH_3(p)$	99·5—100°
	$(p)CH_3\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Cl(p)$	91—92
	$(p)CH_3\cdot C_6H_4\cdot N_3(CH_3)\cdot C_6H_4\cdot Cl(p)$ ..	80—82

The isomerism of these triplets is shown not only by their melting-points, but also by their products of decomposition by cold hydrochloric acid. These products have, in all cases, been examined quantitatively, and the general results are shown by the equations—

1. $X\cdot N_2\cdot NR'\cdot Y + HCl = X\cdot N_2\cdot Cl + Y\cdot NHR'$.
2. $Y\cdot N_2\cdot NR'\cdot X + HCl = Y\cdot N_2\cdot Cl + X\cdot NHR'$.
3. $2X\cdot N_3R'\cdot Y + 2HCl = X\cdot N_2\cdot Cl + Y\cdot N_2\cdot Cl + X\cdot NHR' + Y\cdot NH\cdot R'$

From this it appears that the alkyl-derivatives of the mixed diazoamides always split up, like the unalkylated products, into a mixture of the two diazochlorides and two alkylamines. The most feasible interpretation of these facts is that the *mixed* diazoamides have double the molecular weight usually assigned to them, and in support of this conclusion the authors have discovered that the mixed alkyl-diazoamides can be synthesised by simply boiling the alcoholic solutions of the other two isomerides of the triplet, thus:—

$$X\cdot N_2\cdot NR'\cdot Y + Y\cdot N_2\cdot NR'\cdot X = (X\cdot N_3R'\cdot Y)_2.$$

This observation must necessarily lead to a considerable modification in the existing views respecting the constitution of the diazoamides generally, and experiments in the direction indicated are being carried on both by means of Raoult's method of determining molecular weights as well as by purely chemical methods.

57. "*The Atomic Weight of Zinc.*" By J. H. Gladstone, Ph.D., F.R.S., and Walter Hibbert.

The authors have observed that when amalgamated zinc is used as anode in a zinc sulphate voltameter, the metal dissolved appears to be free from impurity. This they attribute to the electro-chemical relations between zinc and its ordinary impurities, the latter being less readily attacked than the more electro-positive metal. Results obtained in different voltameters with the same current showed a very close agreement, and the authors therefore determined the atomic weight of zinc by applying Faraday's law of electrolysis.

For this purpose a series of copper, silver, and zinc voltameters were arranged in a simple circuit, and the quantity of zinc dissolved was compared with the weights of deposited silver and copper.

The results of five experiments are given, but as two zinc voltameters were employed in each, the data afford ten comparisons of the equivalents of silver and zinc, and eight comparisons of those of zinc and copper. The mean ratio of the equivalents of silver and zinc is 3·298 ± 0·00008. Taking the atomic weight of silver as 107·93, this ratio gives 65·44 as the atomic weight of zinc. If silver is taken as 107·66, zinc = 65·29.

The copper sulphate voltameter is not so accurate as the silver one, owing to the solvent action of the solution on copper. But by keeping the density of the current within certain limits, this action can be made extremely small. Still the ratio Zn : Cu given by the experiments (1·0322) is probably rather higher than it ought to be. There is also uncertainty as to the atomic weight of copper, but the authors have used W. N. Shaw's value, 63·33. This gives 63·33 × 1·0322 = 65·37 as the atomic weight of zinc.

The two comparisons indicate 65·3 as being very near the true value. This is higher than the results obtained in recent years by Marignac, Baubigny, Morse, and Burton, but lower than that given by Reynolds and Ramsay.

58. "*The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water.*" By R. Warington, F.R.S.

Determinations of chlorine and sulphuric acid have been made in the Rothamsted rain-water for several years, and new determinations of ammonia for five years (*Trans.*, 1887, 501); new determinations of nitric acid are now communicated.

The first method employed involved the concentration of 10 lbs. of rain-water with a little magnesia, filtering, and determining the nitric acid as nitric oxide gas by Schloesing's method. This plan gave low results with the stronger rain-waters; the loss apparently took place during the last stage of the concentration, being due to a reduction of a portion of the nitrates by the agency of the organic matter and lead which the water contained.

The method finally adopted involves the reduction of the nitric acid to ammonia by means of the copper-zinc couple. 1 litre of the water is boiled in a retort with magnesia till 250 c.c. have distilled; in the distillate the ammonia present in the water is determined; the residue is diluted to 800 c.c., copper-zinc couple added, and the whole allowed to stand three days at 20—24°; the ammonia present is then determined by distillation and Nesslerising, and its equivalent in nitric acid calculated.

The rain of twenty months, analysed by the copper-zinc method, contained an average of 0·138 of nitrogen as nitric acid per million of water; this is a little higher than that found by Way in 1855—56, namely, 0·12 per million, but is almost identical with that found by Frankland as a mean of his analyses of Rothamsted rain in 1869—70. In a whole year, 1888—89, with a rain-fall of 29·27 inches, the quantity of nitric nitrogen in the rain was 0·917 lb. per acre, and the nitrogen as ammonia 2·823 lbs., or a total of 3·74 lbs. These quantities are compared with those found by other experimenters.

A brief account of the methods employed at Rothamsted in determining the ammonia, chlorine, and sulphuric acid in rain is then given.

59. "*The Product of the Action of Sulphur on Resin.*" By G. Harris Morris, Ph.D.

Pelletier and Walter, in 1838, described a solid hydrocarbon which they separated from the products of the distillation of resin; later observers obtained a similar product by distilling resin with sulphur. The author has examined this latter substance.

The hydrocarbon separates from its solutions in alcohol, benzene, &c., in pale yellow crystalline scales, which melt at 84—85° C.; it boils without decomposition slightly above the boiling-point of mercury. Its composition is expressed by the formula $(C_5H_6)_n$; the density, determined by Victor Meyer's method, using the vapour of sulphur, was 160·07, whilst $(C_5H_6)_5$ requires 165.

From the examination of a number of its derivatives the author concludes that Kelbe is wrong in regarding the substance obtained by the action of sulphur on resin as identical with retene.

60. "*The Vapour-pressures and Specific Volumes of Similar Compounds of Elements in Relation to the Position of those Elements in the Periodic System.*" Part I. By Sydney Young, D.Sc.

Determinations have been made of the vapour-pressures and specific volumes of the four haloid derivatives of benzene, and also of benzene itself, within very wide limits of temperature; benzene, fluobenzene, and chlorobenzene having been heated to their critical points, 288·5°, 286·55°, and 360·8° respectively.

It is shown that if the four haloid derivatives are compared at such temperatures that their vapour pressures are equal, the (absolute) temperatures and also the specific volumes bear a constant ratio to each other, whatever the common pressure.

But on comparing benzene with one of its haloid-derivatives it is found that these simple relations do not hold. The ratios of the absolute temperatures of benzene and fluobenzene corresponding to equal pressures are very exactly expressed by the equation $R' = R + ct$, where R' is the ratio at a pressure for which the corresponding centigrade temperature of fluobenzene is t, R = 0·0838, and c = 0·0000313.

If the specific volumes of benzene and fluobenzene are compared at temperatures corresponding to pressures which are in all cases proportional to the critical pressures of the two liquids, the ratios of the volumes are found to be very nearly constant. If, again, the specific volumes are compared at absolute temperatures which are in all cases proportional to the absolute critical temperatures, the ratios of the volumes are again nearly constant. But the two methods of comparison are not equivalent—though that is stated to be the case by Van der Waals—and they cannot both be correct, for it cannot be taken as even approximately true that the absolute temperatures corresponding to pressures which are always proportional to the critical pressures are themselves proportional to the absolute critical temperatures. Moreover, the values obtained by the two methods of comparison are not quite the same, and for two liquids which are chemically dissimilar, the values may differ considerably. It is impossible at present to say with certainty which method of comparison gives the better results, but the author is inclined to think that the comparison at "proportional" or "corresponding" pressures is most likely to be correct.

The relations of Van der Waals as regards "corresponding" temperatures, pressures, and specific volumes of liquid hold good accurately in the case of the haloid-derivatives of benzene, but the critical pressures of the haloid-derivatives are *equal* and the comparisons must therefore be made at *equal* pressures.

Fluorine, chlorine, bromine, and iodine belong to the same group in the periodic table; the effect of substituting one of these elements for another in the compounds of the type C_6H_5R, as regards the relations between vapour-pressure, temperature, and specific volume, is extremely simple, but if hydrogen be substituted for one of the halogens, the changes produced are much greater.

61. "*The Vapour-pressures of Quinoline.*" By Sydney Young, D.Sc.

Four years ago Dr. Ramsay and the author, in describing their method of obtaining constant temperatures (*Trans. Chem. Soc.*, 1885, 640, and 1886, 37), gave tables of the vapour-pressures of various pure liquids from 0° to 360° C. One of these, methyl salicylate, gives less

satisfactory results than the others, and it is proposed to substitute quinoline for it. Determinations of the vapour-pressures of quinoline are described, and a table is given for each degree between 180° and 240°.

PHYSICAL SOCIETY.

June 8, 1889.

Prof. Ayrton, F.R.S., Vice-President, in the Chair.

Dr. Bond and Mr. Britton were elected Members.

The following communications were made:—

A "*Photograph of Lightning Flashes*" was exhibited and described by Dr. Hoffert.

The photograph was obtained during the storm on the 6th inst., whilst the camera was being waved about in the hands, and shows three similar and parallel flashes, thus proving that successive sparks in multiple flashes may traverse the same path and may be separated by appreciable intervals of time. The supposed primary spark is intersected by numerous tributary ones spreading out on both sides, the second spark shows one tributary, and the third none. Faint bands of light pass across the plate parallel to the direction of motion, and these prove that some residual illumination exists during the intervals between the successive flashes. Evidence of a dark flash is also presented by the plate.

Prof. Herschel, who had taken photographs during the same storm, referred to the fluttering appearance of the flashes and on their long duration; in many cases the time was sufficient to allow him to direct the camera towards the flash and make a successful exposure. He had also observed multiple flashes with the unaided eye, and on waving his hand about he had sometimes noticed about a dozen distinct images of it during one discharge.

Mr. Gregory said that he watched the storm along with two others, and they could seldom agree as to the shape of the flashes, or on their simple or multiple character. The want of agreement as to multiplicity he thought might be caused by their eyes being directed towards different parts of the sky when a multiple flash occurred; the one who happened to be looking towards the flash might be conscious of only one impression, whereas the others, in directing their eyes, would receive the flashes on different parts of the retina. In some cases as many as three distinct flashes (occurring at intervals of about ten seconds) traversed the same path, and a number of the discharges presented a beaded or striated appearance. The beads seemed to remain after the main flash had faded, and this might account for the bands shown in Dr. Hoffert's photograph.

Mr. C. V. Boys, in referring to multiple flashes, said that although his statements made in the discussion of Mr. Whipple's paper on April 13th were not readily accepted, yet no one who watched the recent storm could doubt their existence.

Prof. S. P. Thompson thought the order of the flashes on the photograph may have been the reverse of that supposed, for he observed that the bands of light extended on both sides of the (so-called) primary flash, whereas the outside of the third flash was quite dark.

Mr. E. W. Smith noticed many cases of "sympathetic discharge," in which a flash in the north seemed to precipitate another in the N.W. within a few seconds, and in this he was corroborated by Mr. Gregory, who viewed the storm from a different locality.

Mr. C. V. Burton thought the heating of the air by the first spark of a multiple flash might give rise to the tributary sparks in subsequent ones.

Mr. A. W. Ward mentioned a long flash observed at Cambridge, which passed from the zenith and struck some farm buildings at a distance, and he was particularly impressed by the considerable time occupied in its progress.

"*On the Methods of Suppressing Sparking in Electro-Magnets.*" By Prof. S. P. Thompson, D.Sc.

The object of this paper is to classify the methods which have been suggested, and to draw attention to a novel method of some importance. The classification is as follows:—(1) *Mechanical Devices:* (*a*) simple snap switch; (*b*) break in magnetic field; (*c*) break under liquid; (*d*) wiping breaks (asbestos, &c., brushes); (*e*) blow-out. *Electrical Devices:* (A) use of condensers, (*a*) placed across gap, and (*b*) across terminals of magnet; (B) mutual induction protectors, (*a*) copper sheath around core and (*b*) layers of foil between winding; (C) short-circuit working; (D) differential winding; (E) high resistance shunt (non-inductive); (F) voltameter or liquid resistance across gap; (G) multiple wire arrangement of Mr. Langdon Davies; (H) electro-magnet with two bobbins in series or parallel.

The merits and demerits of the different methods are indicated. The multiple-wire arrangement used by Mr. Langdon Davies in his harmonic telegraph consists in winding each layer separately and uniting all in parallel. The effect of this is to make the time constants of the layers different, and on breaking the circuit the energy is spent in mutual discharges.

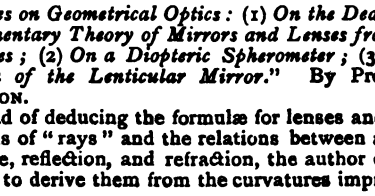
"*A Shunt Transformer.*" By Mr. E. W. Smith.

Two conductors, A and B, of equal impedance, are placed in series between alternate current mains, and the same mains are connected through two incandescent lamps in series. The conductor A has great resistance and B has large self-induction, and when their junction is joined to that of the two lamps both lamps become brighter, and the main current is reduced. These phenomena were shown before the Society. Since A may consist of lamps and B may be a choking coil the arrangement will serve to increase the P.D. between the terminals of the lamps without wasting much energy.

Experiments of a similar nature have been made on a Mordey transformer wound with three equal coils. One coil was used as primary and the other two as separate secondaries, their respective circuits consisting of lamps and an alternate current motor. Under these conditions the arithmetical sum of the mean secondary currents exceeded the primary current by 14 per cent; the secondary volts were 8 per cent less than the primary. All these experiments strikingly illustrate the effects of acceleration and lag in alternate current circuits, and (as was pointed out by the author) show that meters registering "ampère-hours" merely may give readings differing greatly from the numbers representing the energy used.

"*Notes on Geometrical Optics:* (1) *On the Deduction of the Elementary Theory of Mirrors and Lenses from Wave Principles;* (2) *On a Dioptric Spherometer;* (3) *On the Formula of the Lenticular Mirror.*" By Prof. S. P. Thompson.

Instead of deducing the formulæ for lenses and mirrors by means of "rays" and the relations between angles of incidence, reflection, and refraction, the author considers it better to derive them from the curvatures impressed on



waves at the bounding surfaces of the different media. Indices of refraction are replaced by their reciprocals, which express the relative velocities of light, and curvature is measured by the camber at the middle of chords of equal (but small) length. An example will assist in

making the method of treatment clear. Suppose a', a'; a, a; two successive positions of a plane wave front in air, which impinges on a curved surface E A F at A, and let the curvature at A be R and the velocity constant of the substance h. Then, whilst the part a travels in air to b, the part in the denser medium reaches C where $AC = h \cdot ab$ and a curvature, F, represented by B C, is impressed on the wave, which thus converges to at point, Q. Since $AC = h \cdot ab = h \cdot AB$ and—

$$\frac{BC}{AB} = \frac{AB - AC}{AB} \therefore \frac{BC}{AB} = 1 - h,$$

and the relation between the impressed curvature and that of the surface becomes $F = R(1-h)$.

By successive application of the above methods all the ordinary lens problems may be treated, and the resulting expressions are simplified by being expressed in curvatures. The ordinary mirror formula, $f = \frac{r}{2}$ becomes $F = 2R$, and that for the lenticular mirror $F' = 2R + F$. The method readily lends itself to the determination of the changes in the shape of wave-fronts entering or emerging from surfaces of irregular outline.

The diopteric spherometer has its outer feet situated on a circle of 44·71 m.m. radius, and is provided with a screw of 1 m.m. pitch. The instrument so constructed reads off directly in "diopteries," *i.e.*, curvatures expressed on a scale in which that of a sphere of one metre radius is taken as unity.

"*On the Use of the Biquartz.*" By Mr. A. W. Ward.

This is a mathematical investigation into the causes of the varying degrees of accuracy obtained by different observers who have used the biquartz in rotation measurements. Assuming that elliptically polarised light passes through the biquartz, the equation which must be satisfied to give equality of tint on the two halves is shown to be $\cos 2\psi \cdot \sin 2\phi \cdot \sin 2\overline{\omega - \theta} = 0$, where $\tan\psi$ = ratio of axes of ellipse, ϕ = rotation produced by quartz for wave-length λ, θ = angle between plane of vibrations of analyser and that of xx, the axis of x being parallel to the direction of transmission, and ω = angle between one axis of the ellipse and that of x. The equation is satisfied by either $\cos 2\psi = 0$, or $\sin 2\phi = 0$ or $\sin 2\overline{\omega - \theta} = 0$. The first solution relates to circularly polarised light and need not be considered; the second can only hold for one particular wave-length, depending on the thickness of the quartz, and in interpreting the third solution it is shown that a satisfactory result is only obtained when the light is plane polarised. The deductions are in accordance with experiment, for the biquartz has been used with considerable accuracy when experimenting on isotropic media, but with doubly refracting substances, where the light is liable to become elliptically polarised, the results are very discordant.

NOTICES OF BOOKS.

The Uses of Plants: A Manual of Economic Botany, with Special Reference to Vegetable Products Introduced during the last Fifty Years. By G. S. Boulger, F.L.S., F.G.S. London: Roper and Drowley.

This interesting work opens with a historical introduction. Here we learn that in 1838 it was actually proposed to abolish the Kew Botanical Gardens. The author omits, however, to give us the names of the persons responsible for so disgraceful a proposal. He considers that the increased variety of raw vegetable products now imported is due in part to "free trade" and in part to the "International" Exhibitions. We should suspect that the Imperial Exhibition of 1886 would do much more for the introduction of new materials than any of the "International" displays. Nor does he notice the fact that products from the tropical regions, even those forming part of the British Empire, are introduced into continental regions sooner than into this country. Mr. Boulger points out that as so much has been done in economic botany without the aid of science much more may be hoped for from the systematic application of the principles of research. The mention of the nutritive value of the banana reminds us of the difficulty always experienced in introducing any new article of food to the British public. Thus, the yam could be sold here at a lower price than the potato, but, as the author tells us, "it is not appreciated." We believe that it was more frequently used in the last century than it is now.

In speaking of sugars the author omits to state that bees are perfectly able to distinguish beet-sugar from cane-sugar and prefer the latter, and that they repudiate Fahlberg's "saccharine" altogether.

Solanum maglia, from Chili, may, the author hopes, prove capable of general cultivation in Britain as a disease-proof substitute for the potato.

The flavour of pears, it is said, "may be due to iso-amylic acetate,"—a very judicious reservation. If we may judge from their physiological action, the so-called artificial fruit-essences are not identical with the natural flavours of fruits. There is no mention of the billberry, a much more pleasant fruit than the unsweetenable cranberry, rich in gallic acid.

Mr. Boulger deplores with good right the increasing sale of absinthe in Britain. It always seems to us strange that none of our temperance reformers propose the prohibition of its importation and sale.

The artificial vanilla does not seem to have greatly interfered with the cultivation of the natural product. Mention is made of a novel fraud in coffee, its adulteration with or substitution by bad figs, roasted and powdered.

It must not be supposed that this book is of interest merely to botanists. For manufacturers on the look-out for new raw materials it will prove a valuable handy book of reference.

An Elementary Text-Book of Chemistry. By William G. Mixter, Professor of Chemistry in the Sheffield Scientific School of Yale University. Second and Revised Edition. London: Macmillan and Co.

This book, which, though published in London, is evidently and admittedly printed in the United States, presents, at any rate, one feature of distinction from the almost endless array of chemical manuals—it is based upon the periodic classification. Strangely enough we can find in it no mention of the originator of this system, Mr. Newlands! It is scarcely necessary to say that no errors are to be detected in the descriptions of the elements, their compounds, and their reactions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 21, May 27, 1889.

Exact Determination of the Quantity of Water contained in the Blood.—MM. Gréhant and Quinquaud.—In a dog the blood in the femoral vein contains 77·09 per cent of water, whilst that of the femoral artery contains 78·01 per cent. The plentiful introduction of water into the stomach raises the proportion slightly.

Determination of Urea in the Blood and in the Muscles.—MM. Gréhant and Quinquaud.—In 100 grms. of the blood of a rabbit the authors found 35·1 m.grms. of

urea, and in the same weight of the muscles 37·8 m.grms. In another experiment the respective proportions were 98·2 and 107·3 m.grms. Hence they conclude that the urea is formed in the muscles.

The Expansion of Metals at High Temperatures.—H. Le Chatelier.—For all the metals the coefficient of expansion increases with the temperature. The law of increase is generally regular, anomalies having been observed only with some alloys of silver and with all varieties of iron.

Researches on Rotatory Magnetic Polarisation in Iceland Spar.—H. Chauvin.—Iceland spar possesses a rotatory magnetic power not merely along the axis, but also in directions inclined to the axis. Along the axis the magnetic action is a simple rotation of the incident vibration. In directions forming angles with the axis the action of the field generally produces at once a rotation and a transformation of the incident rectilinear vibration into an elliptical vibration. The rotation changes its direction periodically, becoming null for a series of particular directions. These phenomena are identical with those occurring in quartz crystals.

The Electro-conductivity of Saline Solutions. Reciprocal Displacements of Acids.—P. Chroutschoff.—The author's conclusions are that acetic acid is entirely displaced by hydrochloric acid. Sulphuric acid displaces almost entirely tartaric acid in combination with soda, though there are indications of a slight sharing. A sharing takes place between acetic and tartaric acids. But in very dilute solutions the former acid is entirely displaced. In a mixture of sodium acetate and oxalic acid there is a division of the base.

The Electric Resistance of Bismuth.—E. Van Aubel.—Bismuth cannot be obtained pure by chemical processes of precipitation. A determination of the electric conductivity is the most convenient and accurate method of ascertaining the purity of bismuth, and especially the absence of lead. Prof. Classen electrolyses a solution of impure bismuth, when pure metal is deposited at the negative pole and the lead, as peroxide, at the positive pole.

The Combustion-heat of Some Organic Compounds.—J. Ossipoff.—The substances examined in this thermo-chemical paper are racemic acid, hydrated and anhydrous, methyl racemate, and methyl dextro-tartrate.

Some Methods of Producing Mercury-Ammonium Chlorides.—G. André.—The action of dilute ammonia upon a solution of mercuric chloride gives rise either to mercury chloramidide or dimercuriammonium chloride or to a mixture of both compounds. The reaction is different if, along with the mercuric chloride, there is added an equivalent quantity of potash, thus forming yellow mercuric oxide, upon which a solution of ammonium chloride is then poured, or if a portion only of the mercuric chloride is decomposed by potash and ammonia is poured upon the mixture of chloride and oxide. In these cases there is produced, in part at least, tetra-mercuriammonium chloride.

On Certain Metallic Sulphides.—Armand Gautier and L. Hallopeau.—The authors, after referring to a former paper (*Comptes Rendus*, 1889, April 15th) describe the action of carbon disulphide upon nickel, chrome, and lead. In each case a sulphide is obtained. The nickel compound Ni_2S has a metallic appearance and a yellowish lustre. It is absolutely non-magnetic. It does not decompose water, either hot or cold. It is but very slowly attacked by hydrochloric or sulphuric acid. Arfvedson's sulphide, Ni_2S, must have contained metallic nickel. The action of carbon disulphide upon chrome produces the well-known sesquisulphide. The vapours of carbon disulphide convert lead into galena, mixed, at times, with lead sulphocarbonate.

The Presence of Sodium Sulphate in the Atmosphere.—F. Parmentier.—The author traces this fact to the wide distribution of this salt in the soil and to its tendency to crystallise on the surface of porous bodies, whence it is carried away by the wind. An interesting fact mentioned is that if sodium sulphate is allowed to crystallise between plates of unglazed porcelain in the open air, and if the crystallisation is reproduced two or three times by sprinkling with water, the plates fall into powder. The same phenomenon is observed with very hard stones. This crystallisation may be a cause of the comminution of rocks which resist water.

On Cyanacetophenone, Ortho-methyl-cyanacetophenone, and Ortho-toluyl-acetic Ether. General Method of the Synthesis of β-Acetonic Ethers of the Aromatic Series.—A. Haller.—This paper does dot admit of useful condensation.

Action of Potassium upon Triphenylmethane.—M. Hanriot and O. Saint-Pierre.—The authors inquire if the phenyl group, C_6H_5, the presence of which rapidly decreases basicity in the phenylamines, does not suffice to impress acid properties on an adjacent atom of hydrogen.

Determination of Nitric Nitrogen by Means of Ferrous Sulphate.—M. Bailhache.—(See p. 293).

Journal fur Praktische Chemie.
Vol. xxxix., No. 4, 1889.

On Benzyl Acetate and Similar Bodies, Particularly their Behaviour with Chlorine and Bromine.—E. Seelig.—In this memoir the author discusses the substitution of the fatty halogen by acid groups, the action of chlorine upon benzyl acetate, as also that of bromine upon benzyl acetate and parabenzylacetate; the behaviour of chlorine with ethyl benzoate, ethyl acetate, and phenyl acetate; the action of bromine upon phenyl acetate; the behaviour of the esters with hydrochloric acid; and the reaction of chlorine and bromine with toluol.

On Some Di-molecular and Tri-molecular Nitriles.—E. von Meyer.—This paper does not admit of useful abstraction.

On Ortho-nitro-ethyl-aniline and Some of its Derivatives.—A. Hempel.—A preliminary communication.

MISCELLANEOUS.

The London Hospital.—H.R.H. the Duke of Cambridge, K.G., has kindly consented to present to Sir Andrew Clark, Bart., F.R.S., the Senior Consulting Physician of the London Hospital, on July 15, his portrait by the late Frank Holl, which was exhibited at the Royal Academy's Exhibition last year, and subscribed for by the medical and surgical staff and friends of the Hospital. A replica of the painting will, at the same time, be presented to the College. H.R.H. will afterwards distribute the prizes to the Students and the Nursing Probationers.

The Use of Potassium Manganate in Analysis.—Ad. Jolles (*Repertorium der Anal. Chemie*).—An alkaline solution of manganate has the property of forming, in contact with certain metallic oxides, insoluble compounds of constant composition. Upon this reaction the author has founded a method for the volumetric determination of manganese and of cobalt. For determining manganese he adds to a measured quantity of a slightly alkaline solution of potassium manganate the manganous salt in question, constantly shaking the vessel until the supernatant liquid becomes colourless. There is thus produced manganese peroxide free from manganous oxide, which readily subsides, so that the completion of the reaction is distinct. The determination of cobalt is effected in a corresponding manner.

MEETINGS FOR THE WEEK.

Wednesday, 26th.—Society of Arts, 4. (Anniversary).
Thursday, 27th.—Royal Society Club, 6.30. (Anniversary).
Friday, 28th.—Quekett Club, 8.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation (Assignees), have applied for leave to amend the Specification of Letters Patent No. 4415 of 1884 granted to Gerard Wenzeslaus von Nawrocki for "Improvements in the manufacture of colouring matters."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 12th June, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
Comptroller-General.

ABEL AND IMRAY,
Agents for the Applicants,
28, Southampton Buildings, London, W.C.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation (Assignees), have applied for leave to amend the Specification of Letters Patent No. 3724 of 1882 granted to Frank Wirth for "An improved manufacture of certain sulpho-acids and of colouring matters therefrom."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 12th June, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

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THE CHEMICAL NEWS.

Vol. LIX. No. 1544.

THE CONDITIONS OF THE REACTIONS BETWEEN COPPER AND NITRIC ACID.*

By V. H. VELEY, M.A., the University Museum, Oxford.

Introduction.

About fifty years ago De La Rive† observed that pure metallic zinc but slowly enters into reaction with dilute sulphuric acid; shortly afterwards Faraday‡ confirmed this observation in the case of amalgamated zinc. In the course of some investigations on the equivalent of this metal, Ramsay and Reynolds§ failed to obtain any hydrogen from sulphuric acid and samples of zinc which they had purified by every possible precaution. Thus the evolution of hydrogen from zinc and sulphuric acid depends initially upon the presence of some third substance, be it an impurity of the acid or of the metal.

Similarly Russell‖ has also observed that metallic silver is slowly attacked by nitric acid freed from any considerable quantity of nitrous acid, and that the rate with which the change proceeds depends upon the proportion of nitrous acid present.

Reactions between Copper and Nitric Acid.

The changes which take place when metallic copper is dissolved in nitric acid have attracted the attention of a number of investigators; the complexity of these changes and their almost infinite variety produced by slight variations of the conditions, are evidenced by the elaborate researches of Deville,¶ Armstrong,** with Acworth and Divers.†† In the present communication I have the honour of laying before the Royal Society a short and preliminary account of some experiments on the conditions necessary for a reaction to take place between metallic copper and nitric acid.

The Methods of Experiment.

By means of a mechanical device, described fully in another paper before the Chemical Society, spheres of the purest electrotype copper procurable were placed on a small glass dish which was kept continually revolved in dilute nitric acid; a fairly uniform current of carbonic acid was also passed through the liquid to ensure its perfect agitation, and thus to remove the products of the reaction from the immediate vicinity of the metal.

The nitric acid was made up in considerable quantity at a time by diluting acid of sp. gr. 1·41 with a suitable proportion of water; the specific gravity of the diluted acid was taken by means of a very delicate picnometer of the form devised by Sprengel, and the amount of free acid determined in the same portion by the ordinary process of acidimetry. The weight of the copper sphere, as also its diameter, was determined before and after each experiment, which lasted for one hour; from the diameters the mean area of metallic surface exposed was calculated; thus the amount dissolved off per unit area could be directly determined.

In some earlier experiments made with a view of ascertaining this amount, it was noticed that when the sphere of copper was introduced into the acid the evolution of gas did not commence at once, but if, other conditions remaining the same, the sphere was introduced into the acid containing in small quantities the products of the reaction of a former experiment, the evolution of gas commenced immediately. Further, the amount of copper dissolved per unit area was less in the first than in the succeeding experiments, after that the products of the change had been allowed to accumulate in the acid. This will be rendered more evident by the figures given in the table below, the first two columns of which contain the weights of two copper spheres, A and B (placed alternately in the acid), before and after each experiment, the third the differences between these two numbers, the fourth the mean area in square m.m., and the fifth the amounts dissolved off per unit area expressed as decimilligrms. per square m.m. surface, written for the sake of brevity M/A. In this and all succeeding experiments a long-range thermometer was used.

Table I.

Sp. gr. of acid at 19° compared with water at the same Temperature = 1·1699. Percentage of free nitric acid = 27·53. Temperature 25°.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of M/A.
4·4153 (A)	4·0768	0·3385	291·95	11·60
4·5823 (B)	4·2049	0·3774	300·05	12·38
4·0768 (A)	3·7378	0·338	275·83	12·25
4·2049 (B)	3·8465	0·3584	283·16	12·65
3·7378 (A)	3·4166	0·3125	261·23	12·37
3·8465 (B)	3·5268	0·3197	266·78	12·10
3·4166 (A)	3·1188	0·2975	246·52	12·07

It will be seen from the above table that the amount dissolved off per unit area in the first experiment is less than that in the succeeding experiments, when the products of the change were present in the acid.

In another series of experiments the nitric acid used in the first operation was rejected, and another portion of the same sample was taken for the second operation; but for those succeeding this latter was used again. It was observed that in the first two experiments the evolution of gas did not commence immediately after the introduction of the sphere into the acid, whereas in all the succeeding experiments this was the case.

Table II.

Sp. gr. of acid at 19° = 1·1643. Percentage of free nitric acid = 27·02. Temperature 20° C.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of M/A.
4·762	4·6519	0·1102	313·16	3·52
4·6519	4·5451	0·1068	307·29	3·48
4·5451	4·3823	0·1628	300·41	5·42
4·3823	4·2303	0·1520	293·23	5·20
4·2303	4·0838	0·1475	286·77	5·29
4·0838	3·9456	0·1383	280·15	5·05

It will be manifest from the above table that the values for the amount dissolved off per unit area on the first two experiments are concordant among themselves, as also are those of the succeeding experiments, but that those of the former are lower than those of the latter.

When copper is dissolved in nitric acid, the substance more immediately evident to the senses is cupric or cuprous nitrate or nitrite, or possibly a mixture of some of them; at first I was inclined to the belief that the copper salt was the third substance which induced the reaction between the metal and the nitric acid to start at once. Indeed, at a meeting of the Chemical Society I expressed this opinion in the course of a debate.

It was found subsequently that the dilute nitric acid used in the above experiments contained a small trace of nitrous acid. Accordingly a sample of nitric acid of sp. gr. 1·41 was freed from nitrous acid by passing a rapid stream of air through it at a temperature not ex-

* A Paper read before the Royal Society, June 6, 1889.
† *Annales de Chimie*, vol. xliii., 1830, p. 425.
‡ "Experimental Researches," Series VII., p. 863.
§ *Chem. Soc. Journ.*, 1887 (*Trans.*), p. 854.
‖ *Chem. Soc. Journ.*, 1874, p. 3.
¶ *Compt. Rend.*, lxx., pp. 20 and 550.
** *Chem. Soc. Journ.*, 1877, p. 54.
†† *Chem. Soc. Journ.*, 1883, p. 443.

ceeding 35° C.; during the process the acid was protected from direct sunlight. If the temperature rose to 40° C., or the acid was not properly sheltered, nitrous acid was formed by the decomposition of the nitric acid at a rate faster than that at which it was oxidised by the air current. The acid was subsequently diluted with the required quantity of water and preserved in a dark cupboard. When 3—4 c.c. of this diluted acid were mixed with about 100 c.c. of water, no blue colour was produced on addition of starch and potassium iodide solutions, and the faintest possible orange tinge imparted to an aqueous solution of meta-phenylene-diamine-hydrochloride. The acid was thus free from any considerable trace of nitrous acid. Experiments similar to the above were repeated, but the current of carbonic acid omitted, in order to more precisely fix the conditions.

After introduction of a copper sphere there was no evolution of gas for three minutes, and five minutes after that the reaction had set in a considerable quantity of nitrous acid was shown to be present. As regards the production of nitrous from nitric acid under these conditions, Professor Armstrong writes, in a note appended to a paper by Dr. Divers:* "With reference to the formation of N_2O_4 during the dissolution of metals, &c., I some time ago satisfied myself by experiment that it is produced . . . . and there is, I believe, no doubt that, whatever the nature of the reducing agent, be it hydrogen or metal, ... the primary product of the reduction of nitric acid is nitrous acid." This observation, made some time ago, is amply confirmed by the above and succeeding experiments. I would, therefore, merely wish to call attention to the short interval of time which elapses between the commencement of the reaction and the formation in considerable quantities of nitrous acid. Again, when the copper sphere was introduced into the acid containing the copper salt and the nitrous acid, the evolution of gas commenced at once.

In another experiment, in which the copper sphere was previously heated and then allowed to cool in a current of hydrogen to remove any superficial coating of cupric or cuprous oxide, no gas was evolved for 1 min. 50 secs. after the introduction of the sphere into the acid, and 4 min. 30 secs. after the reaction had set in an abundance of nitrous acid was shown to be present.

At this point, Mr. Harcourt, from a recollection of some experiments by the late Sir Benjamin Brodie, suggested to me to place into the acid a substance which should remove the nitrous acid as fast as it might be formed; urea fulfils this requirement, in that it reacts immediately with nitrous acid to form nitrogen and carbonic acid, according to the equation—

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

Accordingly 1 grm. of urea, dissolved in 1 c.c. of water, was added to a litre of nitric acid (sp. gr. $\frac{1}{15}^{8} = 1{\cdot}1662$, percentage of nitric acid = 27·25), into which was also placed 0·9445 grm. of copper nitrate (prepared by dissolving a few of the discarded copper spheres in dilute nitric acid, evaporating the solution over the water-bath, and twice re-crystallising from water). At a temperature of 25° C. no gas was evolved for two minutes after insertion of the copper sphere; it was then taken out, the liquid agitated mechanically, and the sphere again introduced; no gas was evolved for 2 mins. 50 secs. A further quantity of 2 grms. urea, dissolved in 2 c.c. water, was introduced and the experiment repeated; no gas was evolved for 7 min. 30 secs. These experiments show that even in the presence of a small quantity of copper nitrate the addition of comparatively small proportions of urea will temporarily prevent the solution of the copper. It also appeared that when once the reaction had set in it could not be stopped, even though there were present in the acid more than sufficient urea to destroy the nitrous acid which might have been formed. For after agitation of the liquid the copper was again unattacked by the acid. If, then, the apparently purely local formation of nitrous acid could be prevented, it might be possible to prevent also any reaction between the copper and nitric acid from taking place.

To test this point, 1 grm. of urea dissolved in 1 c.c. of water was added to a litre of nitric acid taken from the same sample as that used in the preceding experiments. The little glass dish was more quickly rotated by means of the machine, and a very rapid current of carbonic acid passed in, so that the whole liquid was kept in violent agitation. The copper sphere was introduced, the acid being heated to 25° C. During an interval of *one hour* no gas was evolved, no blue colour imparted to the acid, no alteration of the metallic surface apparent, and the loss in weight experienced was only 0·0025 grm. Whereas, if all other conditions had remained the same, except that the nitrous acid had been initially present and had been allowed to accumulate, the loss of weight from a sphere exposing a surface of 256·85 m.m. would have been about 0·3 grm. (calculated from the results given in Table I., the conditions of the experiments in the two cases being practically identical). This experiment might doubtless have been allowed to proceed for a longer time with the same result.

It shows, I believe, that *pure copper will not dissolve in pure dilute nitric acid*, for though the proportion of nitric acid to that of urea present was, under these conditions, 272·5 : 1, yet the small quantity of the latter was sufficient to completely stop the reaction. It also appears that the dissolution of copper in nitric acid is dependent solely upon the local production of nitrous acid, effected probably by local electric circuits due to traces of impurities in the copper; the proportion of nitrous acid initially produced is possibly also increased by a local rise of temperature. As regards this point Dr. Russell writes (*loc. cit.*):—"The nitrous acid attacks the silver, forming silver nitrite, nitric oxide, and water, the nitric oxide thus formed reducing hydric nitrate, and forming more nitrous acid. Thus the action gets quicker and quicker. The point still remaining to be explained is, then, how the first trace of nitrous acid is formed." My experiments, *mutatis mutandis*, are quite in accord with these observations. To test the matter further, the temperature of the same sample of acid was raised to 30° C., other experiments having shown that the amount of copper dissolved off per unit area is doubled for every 4° C. No gas was evolved for four minutes after the introduction of the copper sphere; it was then taken out, and again introduced, and again no gas was evolved for four minutes. The loss in weight after the eight minutes insertion was only 0·0025 grm., whereas it was calculated that the amount dissolved off during the interval of time, supposing the urea to have been absent, would have been 0·11 grm.

Into the same liquid a further quantity of 2 grms. urea dissolved in 2 c.c. of water was added; the acid was heated to 28—28·2° C., no gas was evolved for eighteen minutes; then, as the supply of carbonic acid accidentally failed, the evolution of gas from the copper started; the loss of weight observed was 0·0015 grm., a quantity which might well have been dissolved off during the interval of time which elapsed between the commencement of the reaction and the removal of the sphere from the acid. During the experiment it was interesting to observe from time to time the formation of a bubble of gas on the metallic surface, which was brushed off by the rotation of the glass dish or the stream of carbonic acid, and consequently any further reaction stopped.

As a further confirmation another sample of acid was made up, containing a slightly greater proportion of free acid, viz., 28·2 per cent, sp. gr. $\frac{1}{15}^{8} = 1{\cdot}1723$; a larger sphere was taken, presenting an area of 322·38 sq. m.m.

The acid was heated to 27° C., and 2 grms. urea dissolved in 2 c.c. water were added. No gas was evolved for fifty minutes, and the loss of weight observed was only 0·0015 grm.

* *Chem. Soc. Journ.*, 1883 (*Trans.*), p. 456.

Several other similar experiments have been made with similar results, which, however, it is not considered necessary to quote.

The conclusions which I venture to think may fairly be drawn from the observations herein described are :—

(i.) The view of Professor Armstrong is corroborated that the primary product of the reduction of nitric acid by copper is nitrous acid; the latter is formed immediately after any chemical change has taken place.

(ii.) If this initial formation of nitrous acid be prevented by suitable means *copper by itself will not dissolve in dilute nitric acid by itself.*

It would follow that the production of nitric acid and nitrous oxides with nitrogen, in proportions varying according to the conditions, is due to subsequent changes occurring between nitrous acid and cupric or cuprous nitrate or nitrite in presence of nitric acid.

I propose to continue these researches, substituting other metals for copper, especially those which are supposed to yield primarily nitrous acid.

In conclusion, I would express my thanks to Mr. Vernon Harcourt for the suggestion which proved of so much value, and to the authorities of the University for affording me facilities for this investigation.

Postscript.—Since the above was written experiments have been made in which the reaction between the copper and dilute nitric acid (sp. gr. = 1·1723), heated to 27° C., was successfully prevented for some time, even in absence of urea, by substituting a current of air for that of carbonic acid.

NOTES OF RECENT AND FUTURE RESEARCH THE SYNTHESIS OF CAFFEINE.

By SAMUEL E. PHILLIPS, F.C.S.

Uric acid, so-called, is no acid at all, and the supposed salts are metal and other replacements in the amide or ureide. It is the strict analogue of xanthine, sarcine, guanine, carnine, and other animal ultimates; and it is interesting to note that we have their close analogues in the vegetable kingdom, in theobromine and caffeine; the former being dimethyl xanthine. All of which proclaim their amide or ureide characters by forming chlorides, sulphates, acetates, &c., &c., of their ammonium forms.

Some time ago Adolph Strecker obtained a silver xanthine with Ag_2 replacing H_2, and by a familiar reaction with methyl iodide, 2AgI were eliminated and the nascent Me_2 assimilated, when the product was proved to be identical with theobromine. On another occasion he obtained a mono-silver theobromine, and treating this with methyl iodide the product was found to be identical with caffeine, thus proving it to be a trimethyl xanthine.

Chemists are familiar with a dimethyl-malonyl-urea,—

$$\left.\begin{matrix} 6\,1\,4 \\ 2\,3 \\ 2\,3 \end{matrix}\right\} = (10\,5\,4),$$

therefore, $(CO)_2C_{10}H_5O_4,H_3N_2$; and this + urea − 4HO would give the elements of theobromine, thus—

$$(CO)_2\,10\,5\,4,H_3N_2+(CO)_2H_4N_2=(CO)_4C_{10}H_5O_4,H_7N_4(a)$$
$$-2HO=(CO)_2Cy\,10\,5\,4,H_5N_3(b)$$
$$-2HO=\quad Cy_2\,10\,5\,4,H_3N_2(c)$$

(*a*) the normal di-ureide; (*b*) the pseudo-uric acid analogue; (*c*) the elements of theobromine.

Now it is an easy problem with chemists to obtain a trimethyl-malonyl-urea ($C_{12}H_7O_4$); and this + urea − 4HO = the elements of caffeine, thus—

$$(CO)_2\,12\,7\,4\,H_3N_2+(CO)_2H_4N_2=(CO)_4\ C_{12}H_7O_4H_7N_4(a)$$
$$-2HO=(CO)_2Cy\,12\,7\,4\,H_5N_3(b)$$
$$-2HO=\quad Cy_2\,12\,7\,4\,H_3N_2(c)$$

(*a*) the normal diureide; (*b*) the pseudo-uric acid analogue; (*c*) the elements of caffeine.

The only point of novelty or originality in this contention is the fact of ureas or carbonyl bodies—2HO—giving cyanogen; but this is so abundantly elucidated in the papers referred to under uric acid that it ought to be accepted.

Another fact of much interest which is wholly obscured by the skittle-playing types of modern theory is the unimpaired radical persistence through all the complex changes of M. Grimaux's numerous ureides. In some cases 2, 3, or 4 atoms of acid are combined with 2, 3, or 4 atoms of urea, and every item of these empirical syntheses strictly corresponds with the views we are seeking to enforce.

In conclusion we cite two of the simplest cases. M. Grimaux has synthesised allantoin and pyruvil, and has the penetration to see that both should have similar constitutions. We find them both one stage short of the ultimate and therefore pseudo-uric acid analogues—

Allantoin is from glyoxalic acid + urea, thus—

$$(C_4H_1O_4)O.HO+(CO)_2H_4N_2-2HO=(CO)_2\,4\,1\,4\,H_3N_2(a)$$
$$(a)+(CO)\ H_4N_2=\quad (CO)_4\,4\,1\,4\,H_7N_4(b)$$
$$-2HO=\quad (CO)_2Cy\,4\,1\,4\,H_5N_3(c)$$
$$-2HO=\quad Cy_2\,4\,1\,4\,H_3N_2(d)$$

(*a*) Glyoxal urea, miscalled allanturic acid; (*b*) the normal diureide; (*c*) allantoin; and (*d*) the ultimate amide or cyanamide, miscalled mycomelic acid.

That (*c*) really is a cyanamide is proved by the fact that it may be produced by the direct union of glyoxal urea (*a*) with cyanamid.

Pyruvil is from pyruvic acid + 2 urea, thus—

$$6\,3\,4,O.HO+(CO)_2H_4N_2-2HO=(CO)_2\ C_6H_3O_4H_3N_2(a)$$
$$(a)+(CO)_2H_4N_2=\quad (CO)_4\ \ 6\ 3\ 4\,H_7N_4(b)$$
$$-2HO=\quad (CO)_2Cy\,6\ 3\ 4\,H_5N_3(c)$$
$$-2HO=\quad Cy_2\,6\ 3\ 4\,H_3N_2(d)$$

(*a*) Pyruvic urea, probably not yet obtained (M. Grimaux's pyruvil urea is acid + urea − 4HO, which must be a cyanamide, Cy 6 3 4 HN); (*b*) the diureide; (*c*) pyruvil; and (*d*) the ultimate not yet obtained.

Wokingham Road, Reading,
May 25, 1889.

ON DIACETYL AND SOME OF ITS DERIVATIVES.*

By HARRY F. KELLER.

With a view to a synthetic formation of citric acid, Fittig and Daimler† subjected ethyl oxalate to the action of ethyl monochloracetate and zinc. The reaction did not take place in the desired manner, but they found among the products the ether of a dibasic diketonic acid, which they termed ketipic (diketoadipic) acid. From the reactions of this ether it appeared highly probable that the structure of the acid must be expressed by one of the two formulæ:

CO,CH_2COOH	$CO,CH_2,COOH$
CO,CH_2COOH	$CH_2,CO,COOH$

It was observed that upon heating the acid was decomposed into carbonic dioxide and a yellow volatile liquid. At the suggestion of Professor Fittig I undertook the study of this reaction in the hope of arriving at a definite conclusion in regard to the structure of ketipic acid. The former of the two formulæ given above proved to be correct; ketipic acid is readily split up into diacetyl and carbonic anhydride according to the equation—

$$\begin{matrix} CO,CH_2,COOH \\ CO,CH_2,COOH \end{matrix} = \begin{matrix} CO,CH_3 \\ CO,CH_3 \end{matrix} + 2CO_2$$

* From the "Inaugural Dissertation for the Degree of Doctor of Philosophy," Strassburg, 1888. Chemical Section of the *Journal of the Franklin Institute*, April, 1888.

† *Ber.*, xx., 202.

Diacetyl is the simplest orthodiketone of the fat series, a class of compounds for the production of which a great many fruitless attempts have been made. Since the discovery of its formation from ketipic acid, diacetyl has been obtained by two other reactions, viz.: (1) By V. Pechmann,* on treating isonitrosomethylacetone successively with acid sulphites of the alkalies and dilute sulphuric acid, and (2) by L. Wolff,† who found that it was formed by boiling β-dibrom-lævulinic acid with water.

The constitution of diacetyl is deduced from the following facts:—

(1). Its empirical formula is $C_4H_6O_2$.

(2). It combines readily with two molecules of phenylhydrazine, of hydroxylamine, and of hydrocyanic acid. It must, therefore, contain twice the carbonyl group.

(3). As the dicyanhydrin yields dimethylracemic acid, the two carbonyl groups must be directly united.

Preparation.—In order to obtain a sufficient quantity of diacetyl for investigation, it was necessary to prepare large quantities of ketipic ether. In the beginning the method described by Daimler‡ was strictly adhered to, while later it was found more convenient to prepare it according to W. Wislicenus's§ reaction from ethyl acetate, ethyl oxalate, and metallic sodium. The ether was converted into the free acid by treating it in the cold with hydrochloric acid saturated at 0°; small quantities of it that had escaped saponification were removed by boiling the dry powdered product with chloroform, in which the acid is insoluble.

From this acid diacetyl can be obtained either by destructive distillation or by boiling with dilute sulphuric acid.

In decomposing ketipic acid in the dry way it was found necessary, for obtaining a satisfactory yield of the diketone, to distil *small* quantities, not exceeding five grms. at a time and to heat rapidly. The escaping vapours and gases were passed through a U-tube, provided below with a collecting bulb, and at the farther limb with an inverted condenser. The U-tube and bulb were placed in ice. The heating is continued until white fumes cease to come off. In the receiver there collects a liquid which consists of two layers: the upper one, which is of an oily appearance, is almost pure diacetyl, and the lower one, an aqueous solution of it. They were separated by means of a tap funnel, and sodium chloride added to the watery solution. Diacetyl and very little water passed over first on distillation. The oily layers were then united, dried with neutral chloride of calcium, and fractioned. The by far greater portion distilled over between 85° to 89°, and but a small reddish brown residue of empyreumatic odour remained in the bulb. The distillate showed a much lighter colour than the original product; it was again treated with chloride of calcium, and then distilled over completely between 87·5° and 88°.

The decomposition of ketipic acid is also readily effected by heating with dilute sulphuric acid (1 : 10). A violent evolution of carbonic anhydride is observed when the liquid is heated to near its boiling-point, and great care must be exercised in regulating the temperature in order to avoid serious losses. The aqueous distillate is treated as described above.

The yield never exceeds fifty per cent of the theory; it is about the same for both methods.

All attempts to obtain the monocarboxylic acid of diacetyl by splitting off only one molecule of carbonic acid were unsuccessful.

Diacetyl is a mobile liquid of an intensely yellow colour and characteristic odour. It boils without decomposition between 87·5° and 88°; the vapour is greenish yellow, resembling chlorine. Its specific gravity is ·9734 at 22°. It is soluble in four parts of water at ordinary temperature, and is miscible with alcohol and ether in all proportions.

I. 0·2563 grm. gave 0·5207 grm. CO_2 and 0·1632 grm. H_2O.

II. 0·2150 grm. gave 0·4390 grm. CO_2 and 0·1386 grm. H_2O.

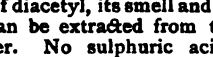
	Calculated for $C_4H_6O_2$.	Found. I.	Found. II.
C	55·81	55·40	55·68
H	6·98	7·07	7·16

Diacetyl prepared by the reactions of V. Pechmann and of L. Wolff was found, on comparison, to be identical in every respect with that from ketipic acid.

Diacetyl shows all the reactions which are peculiar to the ketones. It combines with the acid sulphites of the alkalies with the evolution of heat. The compound formed was not isolated, as it did not crystallise out of the solution upon standing.

When sulphurous anhydride is passed into an aqueous solution of diacetyl, its smell and colour rapidly disappear; nothing can be extracted from the solution by shaking with ether. No sulphuric acid is produced by the reaction, and on evaporating the liquid over sulphuric acid *in vacuo*, diacetyl is regenerated. It is probable that a loose combination of the diketone with SO_2 exists which breaks up as soon as the excess of the latter is removed.

Osazone of Diacetyl.—

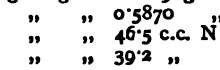


On adding two mols. of phenylhydrazine to the ethereal solution of one mol. of diacetyl, the osazone separates out on standing in the form of beautiful yellowish needles. This compound is insoluble in most of the ordinary solvents, soluble with difficulty in $CHCl_3$, somewhat more readily in acetone, and in boiling benzol. It was obtained pure by re-crystallisation from the latter as a light yellowish powder, melting at 239°, with decomposition.

I. 0·3017 grm. gave 0·8009 grm. CO_2 and 0·1882 H_2O.
II. 0·2213 „ „ 0·5870 „ „ 0·1401 „
I. 0·2579 „ „ 46·5 c.c. N at 17·5° and 751 m.m.
II. 0·2133 „ „ 39·2 „ „ 18° „ 750 „

	Calculated for $C_{16}H_{16}N_4$.	Found. I.	Found. II.
C	72·18	72·38	72·32
H	6·76	6·93	7·03
N	21·06	21·02	21·38

Dioxim.—



This compound is formed by mixing aqueous solutions of diacetyl and of hydroxylamine hydrochloride, which has previously been neutralised with carbonate of sodium. It is precipitated white in the form of microscopic needles. It is insoluble in water, readily soluble in alcohol and ether, and melts with partial sublimation at 234·5°. By boiling it with dilute sulphuric acid, diacetyl is again produced.

0·2380 grm. gave 0·3606 CO_2 and 0·1525 grm. H_2O.
0·2278 „ „ 45·7 c.c. N at 8° and 759 m.m.

	Calculated for $C_4H_8N_2O$.	Found.
C	41·38	41·32
H	6·90	7·11
N	24·14	24·48

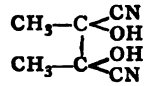
A compound prepared by Schramm* in the laboratory of V. Meyer several years ago, was found to be identical

* *Ber.*, xx., 3, 162.
† Private communication.
‡ "Inaug. Diss.," Strassburg, 1886.
§ *Ber*, xx., 590.

* Schramm, *Ber.*, xvi., 179.

with this dioxim after a re-determination of the melting-point.* It had not been analysed.

Dicyanhydrin.—

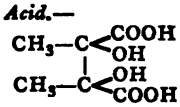


This is obtained by adding diacetyl to an excess of prussic acid in aqueous solution. The mixture is gently warmed for some time and then extracted with ether. On evaporation of the latter, the nitrile remains in the form of colourless needles or prisms, united to peculiar dendritic shapes. It is soluble in water, alcohol, and ether, insoluble in all other solvents. It is very hygroscopic, and decomposes when heated with water. It melts at about 110°.

0·3189 grm. dried in the desiccator gave 57·9 c.c. N at 19° and 734 m.m.

	Calculated for $C_6H_8N_2O_2$.	Found.
N	20·00	20·58

Dimethylracemic Acid.—



Strecker† has observed that racemic acid is formed upon boiling glyoxal, prussic acid, and dilute hydrochloric acid. It was, therefore, to be expected that diacetyl, under similar conditions, would give dimethylracemic acid.

An acid of the composition $C_6O_6H_{10}+H_2O$, and whose properties closely resemble those of racemic acid, was obtained by slightly modifying Strecker's method. It was prepared in the following manner:—The finely powdered crystals of the hydrocyanide were placed in a small flask, and covered with concentrated hydrochloric acid; it passed slowly into solution, but on standing, colourless crystals were observed to separate; they probably represent the acid amide. No attempt was made to determine their character, but the mixture was first heated and then the hydrochloric acid evaporated on the water-bath; the residue was dissolved in water, and the solution divided into two equal parts. Of these one was exactly neutralised with K_2CO_3, and boiled; the other portion was then added. Upon cooling, the acid potassium salt, which—like that of tartaric acid—is difficultly soluble, crystallised out. This was re-crystallised, then converted into the neutral salt, and the solution of this precipitated with acetate of lead. The lead salt was washed with water, dried, pulverised, and then suspended in water and decomposed with hydrogen sulphide. On evaporating the filtrate the new acid crystallised out in large shining prisms and plates. These have the habitus of crystals of racemic acid. They contain one mol. of H_2O, but do not effloresce in the air. The acid is readily soluble in water and in alcohol, insoluble in ether.

0·2494 grm. of air-dry acid gave 0·0227 grm. loss, and 0·3361 CO_2, and 0·1177 CO_2.

	Required for $C_6H_{10}O_6+H_2O$.	Found.
C	36·73	36·75
H	5·10	5·24
H_2O	9·18	9·10

The anhydrous acid melts at 180°; it is decomposed at this temperature. Heated on platinum foil, it is decomposed and completely volatilised without leaving a trace of carbon.

Böttinger‡ has described, as dimethyltartaric acid, an acid which he obtained as a side product by the action of zinc upon an alcoholic solution of pyruvic acid. It showed no tendency to crystallise, undoubtedly because it was impure; its salts are certainly identical with some of those described below.

Potassium Salts.—The neutral salt is obtained from the acid one by exact neutralisation with potassium carbonate. It is quite soluble in water, and crystallises in needles.

The acid salt, $C_6H_9O_6K$, the preparation of which has been described above, is readily soluble in hot water, sparingly in the cold. It crystallises in crusts or little plates. It contains no water of crystallisation.

0·2526 grm. gave 0·1008 grm. K_2SO_4.

	Required for $C_6H_9O_6K$.	Found.
K	18·05	17·92

Calcium Salts.—$C_6H_8O_6Ca+1\frac{1}{2}HO$.* Chloride of calcium throws down from solutions of the neutral salts of the alkalies a white crystalline precipitate, insoluble in water and acetic acid.

0·2653 grm. lost on heating to 215—220° 0·0282 grm. H_2O, and gave 0·1483 grm. $CaSO_4$.

	Calculated for $C_6H_8O_6Ca+1\frac{1}{2}H_2O$.	Found.
H_2O	11·11	10·64
Ca	16·46	16·43

Barium Salt.—$C_6H_8O_6Ba+H_2O$. Although quite as insoluble as the calcium salt, this is not precipitated immediately by barium chloride or acetate; it separates out completely after some time in the form of small needles, which are generally grouped around a common centre. It contains two mols. of water, which are driven off at 160°.

0·2046 grm. gave 0·0211° loss and 0·1364 grm. $BaSO_4$.

	Required for $C_6H_8O_6Ba+2H_2O$.	Found.
Ba	39·25	39·19
H_2O	10·32	10·31

The lead salt is precipitated in the form of a voluminous precipitate on adding lead acetate to the neutral potassium salt solution. It is likewise insoluble in water and in acetic acid. From acid solutions it is obtained in small needles.

In addition to the reactions described, the solution of potassium dimethylracemate gives the following:—$ZnSO_4$ produces a white amorphous precipitate, insoluble in water and dilute acetic acid. $AgNO_3$ in concentrated solutions gives a white curdy precipitate. With ammoniacal silver solutions a metallic mirror is formed, especially on warming.

$HgCl_2$ throws down a white precipitate.

$CuSO_4$ is coloured deep blue by the solution; the liquid remains clear on adding alkalies.

Ferric chloride produces a voluminous yellowish brown precipitate.

Halogen Derivatives of Diacetyl.—Bromine acts upon diacetyl but slowly in the cold; on warming, two atoms of hydrogen are replaced. Dibromdiacetyl is best prepared by adding bromine dissolved in CS_2 or $CHCl_3$ to a similar solution of the diketone until the red colour no longer disappears on heating in the water-bath. The solvent is then distilled off and the residue repeatedly crystallised from carbon disulphide and from petroleum ether. Thus obtained, it forms yellow leaflets of a waxy lustre, melting at 117°. It is soluble in ether, carbon disulphide, chloroform, and petroleum ether.

I. 0·2 grm. gave, after treating with Na amalgam, 3·3083 grm. AgBr.

II. 0·2 grm. gave, after boiling with Na_2CO_3 solution, 0·3079 grm. AgBr.

* Private communication of Professor Meyer to Professor Fittig.

† *Zeitschrift fur Chem.*, 1868, 216.

‡ *Annalen*, clxxviii., 315.

* Both the Ba and Ca salt were dried in the desiccator before they were analysed; for this reason the Ba salt was found to contain less H_2O than Böttinger determined.

	Calculated for $C_5H_6Br_2O_2$.	Found. I.	Found. II.
Br	65·57	65·59	65·51

It is probable that the two atoms of bromine are attached to two *different* carbon atoms, as the action of Br does not seem to proceed any further even when a large excess is added.

Monochlordiacetyl.—By the action of chlorine upon diacetyl in the sunlight, a thick oily liquid, possessing the colour of diacetyl and a pungent smell, was obtained; it did not crystallise at −12°. Its boiling-point is about 150°. Sodium carbonate solution decomposes it, especially on heating.

0·5656 grm. gave, after treating with Na_2CO_3, 0·6566 grm. AgCl.

	Required for $C_5H_5O_2Cl$.	Found.
Cl	29·46	28·72

The further study of the halogen derivatives of diacetyl is being proceeded with.

Metallic Compounds.—When diacetyl is added to a solution of silver nitrate with just enough ammonia to hold the oxide of silver in solution, metallic silver is precipitated, sometimes as a mirror upon the glass; if, on the other hand, a large excess of ammonia be used, a voluminous white precipitate is formed, even in extremely dilute solutions of the diketone. A similar precipitate forms in ammoniacal solutions of cuprous chloride.

After drying them at 100° these substances were analysed with the following results:—

Ag Compound—

I. 0·234 grm. gave 0·2874 CO_2, and 0·892 H_2O, and 0·1153 Ag.

II. 0·2368 grm. gave 0·2898 CO_2, and 0·0923 H_2O.

III. 0·294 grm. gave 0·1442 Ag.

	Required for $C_6H_9N_2Ag$.	Found. I.	Found. II.	Found. III.
C	33·18	33·46	33·37	—
H	4·14	4·23	4·33	—
Ag	49·77	49·28	—	49·04

Copper Compound—

I. 0·2123 grm. gave 0·3216 CO_2 and 0·1030 H_2O.

II. 0·4335 grm. gave 58·6 c.c. N at 15·5° and 755 m.m.

III. 0·2008 grm. gave 0·091 CuO.

	Required for $C_6H_9N_2Ag$.	Found. I.	Found. II.	Found. III.
C	41·86	41·39	—	—
H	5·23	5·35	—	—
N	16·27	—	16·32	—
Cu	36·62	—	—	36·14

These compounds are quite stable; at high temperatures they are decomposed with formation of acetamide.

They are evidently salts of the trimethylglyoxaline, discovered by v. Pechmann.* This was proved also by preparing the hydrochloride of the base, by decomposing the salts with hydrochloric acid, and evaporating the filtrate. The residue was re-crystallised from alcohol-ether.

0·2275 grm. gave 0·2219 AgCl.

	Calculated for $C_6H_{10}N_2HCl$.	Found.
Cl	24·38	24·13

The free base was liberated with sodium carbonate and extracted with ether. Re-crystallised from a mixture of ether and ligroin, it forms small white needles, which have a bitter taste and melt at 130 or 131°.

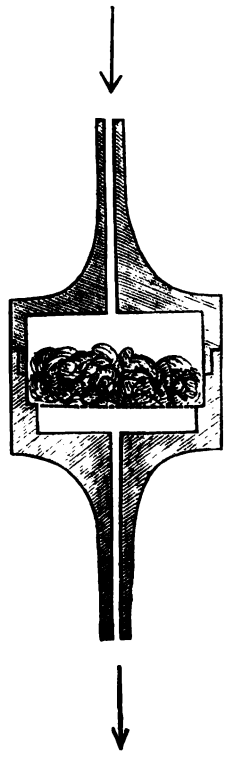
* *Ber.*, xxi., 1411.

AN IMPROVED APPARATUS FOR USE IN DRYING COMBUSTION-TUBES.

By AUGUSTUS E. DIXON, M.D., F.C.S.,
Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

The ordinary method of drying tubes for use in combustion analysis, by heating in a gas or other oven, and withdrawing the contained air at intervals, is tedious and open to the objection that dust is very apt to be introduced. The method of passing the tube backwards and forwards through a large gas-flame, while a current of air is maintained through the former by means of a foot-blower, though rapid and otherwise efficient, is still more open to the objection stated; for the footblower is necessarily placed upon the floor, whence it readily picks up the lighter particles of solid matter which are near the valve.

I enclose a rough sketch of a simple piece of apparatus by which the entrance of dust into the combustion-tube



is completely prevented, while the advantage of using the footblower is retained. It consists of a box of the form shown in the figure, turned out of boxwood, and made in two corresponding pieces, one half fitting air-tight into the other. A disc of wire-gauze is inserted near the distal opening, and the space on the proximal side of the disc packed with clean cotton-wool. The inlet tube is connected with the delivery-tube of the footblower, while the exit-tube is attached to a clean piece of rubber tubing about six feet long. The latter, in turn, is connected with the long narrow glass tube which is used in blowing out the moisture from the heated combustion-tube. These three—filter, rubber tube, and glass tube—are kept exclusively for the purpose alluded to, and are ready for use at a moment's notice.

I have had the apparatus for some time in use, and find that it works very satisfactorily.

THE REDUCTION OF BARIUM SULPHATE TO BARIUM SULPHIDE ON IGNITION WITH FILTER-PAPER.

By CHARLES W. MARSH.

In reading on the subject of some barium salts, while looking over the preparation of barium sulphide by means of igniting the mineral barite with coal and extracting the barium sulphide with water, my attention was again called to the reduction of barium sulphate precipitates by the carbon of the filter-paper on ignition in the regular method for estimation of sulphur. I have noticed in some text-books on quantitative analysis the direction to separate the precipitate of barium sulphate from the filter, ignite the filter, and burn to ash, moisten the mass with sulphuric acid to transform any barium sulphide formed by reduction of the carbon of the filter to sulphate, drive off excess of acid, and ignite again. The precipitate previously separated is now added, and the whole ignited and weighed. I could find no literature on the reduction of barium sulphate by ignition with the filter in the determination of sulphur, and have therefore made the experiments herein described.

Two series of experiments were conducted.

In the first case the method of procedure was as follows:—25 c.c. concentrated sulphuric acid were diluted to 500 c.c. and it was with this acid that all the experiments were made. The diluted sulphuric acid was taken instead of a soluble salt to avoid as much as possible liability of error from incomplete washing. For the first ten determinations various amounts of the acid were further diluted with distilled water, heated to boiling, and barium chloride solution added, and allowed to stand several hours or over night. The precipitates of barium sulphate were repeatedly washed with water by decantation and on the filter until the filtrates gave no reaction for hydrochloric acid. After drying the precipitates the filters were folded over, enveloping them, and cautiously ignited in a platinum crucible with the lid on until the escaping gases were ignited, when the burner was removed. When the flame went out the burner was again applied and the crucible brought to a red heat. The cover was removed, the crucible placed in a horizontal position, and heated until the filter was burned to an ash, cooled, and weighed.

A little water was then added to the contents of the crucible and the whole well stirred, and allowed to settle and the liquid decanted on a filter. In many cases hydrogen sulphide was detected after the addition of water by its odour, and by turning lead acetate paper brown. After having extracted two or three times with water, 2 c.c. of dilute hydrochloric acid were added in small portions with addition of water, whereupon, in most cases, the evolution of hydrogen sulphide was still more pronounced. The precipitate was further treated with water. If there was an odour of hydrogen sulphide in the filtrate a few drops of bromine water were added, and the solution boiled to expel the excess of bromine. A little of the diluted sulphuric acid was added, allowed to stand several hours, and the precipitate of barium sulphate collected on a filter, washed, dried, ignited, moistened with concentrated sulphuric acid, and the barium sulphate ignited and weighed.

This precipitate was derived from the barium sulphide formed by reduction of the barium sulphate by the carbon of the filter-paper during ignition, and was dissolved by the water and dilute hydrochloric acid added, and re-precipitated by sulphuric acid.

The total washings varied between 15 and 20 c.c.

The following table shows the results obtained by working in the manner described:—

	A.	B.	C.	D.	E.
1.	0·9844	0·0068	0·0048	0·9864	0·67
2.	1·0291	0·0073	0·0053	1·0311	0·70
3.	0·9926†	0·0377	0·0273	1·003	3·75
4.	1·0287†	0·025	0·0181	1·0356	2·41
5.	0·9634*	0·0071	0·0051	0·9654	0·73
6.	1·1462†	0·0915	0·0663	1·1714	7·81
7.	1·532†	0·0483	0·0350	1·5453	3·12
8.	1·9413†	0·0679	0·0492	1·96	3·46
9.	1·788*	0·0127	0·0092	1·7915	7·08
10.	1·9247	0·1503	0·109	1·966	7·64
11.	0·2166	0·0021	0·0015	0·2172	0·96
12.	0·1526	0·0012	0·0008	0·153	0·78
13.	0·076†	0·0147	0·0106	0·0801	18·32
14.	0·1621†	0·0039	0·0028	0·1632	2·38
15.	0·0919†	0·006	0·0043	0·0936	6·41

Explanation:—

A = weight of $BaSO_4$ and BaS after ignition in the crucible.

B = weight of $BaSO_4$ obtained by dissolving out BaS and precipitating the barium as sulphate.

C = the weight of $BaSO_4$ found in B, calculated to BaS, from which it was obtained.

D = the weight of A if it were all $BaSO_4$, obtained by subtracting the weight calculated in C from the weight of A, and adding to the remainder the weight given at B.

E = percentage of $BaSO_4$ reduced, found by dividing B by D and multiplying by 100.

Schleicher and Schüll's ashless filter-paper, number 590, was used.

In the first ten experiments the diameter of the filter was 9 c.m., and in the last five 5½ c.m.

The barium sulphate used on the last five experiments as well as in the second series was prepared in one beaker and carefully washed. This saved the individual washings for several precipitates, at the same time giving a precipitate identical in all cases.

The next set of experiments was made in similar manner with this change in manipulation. The ignition of the precipitate was performed without the lid on the crucible, thus giving complete access of air, and more nearly approaching the ignition of barium sulphate as carried out in the determination of sulphur. The results are as follows:—

	A.	B.	C.	D.	E.
16.	0·1389	not reduced			
17.	0·0631	,, ,,			
18.	0·061	,, ,,			
19.	0·0547†	0·0015	0·0010	0·0552	2·71
20.	0·0513†	0·0024	0·0017	0·0520	4·61
21.	0·0654	0·0003	0·002	0·0655	4·59
22.	0·0514	0·0006	0·004	0·0516	1·12
23.	0·0545†	0·0011	0·0008	0·0548	2·00
24.	0·0585†	0·0012	0·0008	0·0589	2·04
25.	0·0598*	0·0057	0·0041	0·0614	9·28
26.	0·7423†	0·0069	0·005	0·7442	0·92
27.	0·7437†	0·0059	0·0042	0·7454	0·79
28.	0·6776†	0·0122	0·0088	0·681	1·79
29.	0·5042†	0·0142	0·0103	0·5081	2·79
30.	0·77†	0·0143	0·0103	0·774	1·84

In the above experiments a filter of 5½ c.m. diameter was used in each case but the last five, where one of 9 c.m. diameter was used. The average reduction in the first table was 4·41 per cent of the barium sulphate originally present, and in the second 2·29 per cent, a trifle more than one half of that in the first case.

A blank experiment was made on 0·8582 grm. barium sulphate with the same amount of hydrochloric acid and water, and but three-tenths of a m.grm. of barium sulphate were obtained. I have not included this in connection with the above table as it is so small.

* Odour of hydrogen sulphide when acid was added.

† Odour of hydrogen sulphide on addition of water, with more evolution on addition of acid.

The before mentioned experiments prove conclusively that there is quite an appreciable amount of barium sulphate reduced by the filter-paper in ignition, and that the reduction is about twice as much when the ignition is made with the cover on the crucible as when made without it.

The moistening of the ignited precipitate of barium sulphate with sulphuric acid and again treating should not be omitted in determination of sulphur as already proved.—*Journal of Analytical Chemistry*, Vol. iii., Part 2, April, 1889.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, June 7th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, the whole were found to be clear, bright, and well filtered.

The character of the metropolitan water supply during the month of May did not present any noteworthy variation from that recorded now for several months past as being entirely satisfactory; but what variation did present itself for notice was in the direction of an increased degree of uniformity of composition among the different samples examined, of an increased degree of freedom from organic matter, and of an increased degree of freedom from colour-tint. For it is to be noticed that the water supply, although, save on rare exceptional occasions, practically colourless, is yet found, when examined quantitatively by the calorimeter, to approximate more closely to entire freedom from colour at some seasons than at others. Thus taking, for convenience of comparison, the water furnished by the five companies taking their supply from the Thames, whereas the mean ratio of brown to pure blue tint in April was as 17 : 20, in the past month it was as 14 : 20 only. Similarly the mean proportion of organic carbon in the same water, which in the first three months of the year amounted to 0·164 part, and had become 0·154 part in April, was found to be further diminished to 1·144 part, in 100,000 parts of the water, in May; with a maximum amount of organic carbon in any one sample examined in May of 0·155 part, as against a maximum of 0·164 part in any one sample examined in April.

The mean composition of the supplies of Thames water delivered by the different companies was practically identical. As usual, the mean proportion of organic carbon in the East London Company's supply derived from the Lea was somewhat below even the small proportion present in the water derived from the Thames; while the mean proportion present in the New River Company's supply of mixed Lea and spring water was appreciably lower still.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE ESTIMATION OF THE TOTAL ORGANIC NITROGEN IN WATER BY THE KJELDAHL PROCESS.

By HENRY LEFFMANN and WILLIAM BEAM.

CHEMISTS will note with much satisfaction, through the recent communication of Messrs. Drown and Martin,* the successful application of the Kjeldahl method to the determination of the total organic nitrogen existing in waters. The so-called albumenoid ammonia process has never been more than a relative determination, and the estimation by the usual combustion method does not seem to be susceptible of general employment in this field. For the benefit of those unfamiliar with the article in question, we present the following abstract:—

Five hundred c.c. of the water are poured into a round-bottomed flask of about 900 c.c. capacity, and boiled until 200 c.c. have been distilled off. The free ammonia which is thus expelled may, if desired, be determined by connecting the flask with a condenser. To the remaining water in the flask, after cooling, is added 10 c.c. pure concentrated sulphuric acid. After shaking, the flask is placed in an inclined position on wire gauze, and boiled cautiously in a good drawing hood until the water is driven off and the concentrated sulphuric acid is white or a very pale yellow. The flask is then removed from the flame, and a little powdered potassium permanganate added until, on shaking, the liquid acquires a green colour. If the colour is purple instead of green, it shows that the water has not been all driven off. After cooling, 200 c.c. of water free from ammonia are added, the neck of the flask being washed free from acid, and then 100 c.c. of sodium hydroxide (200 grms. per litre). The flask is connected with a condenser, shaken to mix the contents, and distilled. The first 50 c.c. are condensed in very dilute hydrochloric acid free from ammonia. The total distillate is made up to 250 c.c., mixed, and 50 c.c. taken and Nesslerised. A correction for the nitrogen in the chemicals used is made by means of a blank experiment. From the experiments made, Drown and Martin conclude that the nitrates and nitrites do not interfere with the accurate determination of the organic nitrogen, the error which might otherwise be caused disappearing under the conditions of great dilution which exist in natural waters.

Numerous observations have established the fact that the organic matter of water is susceptible of decomposition or volatilisation by simple boiling, often in such a manner that a notable proportion of the nitrogen is lost. It appeared, therefore, in experimenting on this process, that it would be advantageous to add the acid at once, and thus obtain the nitrogen existing as organic matter and also in ammonium compounds, estimating that existing in the latter in a separate sample by direct Nesslerising without distillation; the calcium and magnesium, which would otherwise interfere with the colour reaction, being removed by the addition of sodium carbonate and hydroxide, according to the suggestion of

* *Technology Quarterly*, ii., 3.

Morgan. The same principle can be extended to the determination of the ammonium formed by the sulphuric acid. Instead of distilling the liquid after rendering it alkaline, a little sodium carbonate may be added, allowed to stand, filtered, and the filter Nesslerised. In this way the troublesome distillation is avoided. The procedure is as follows:—

Reagents Required.—Concentrated sulphuric acid as free as possible from nitrogen; that which we used was of the same make (Baker and Adamson) recommended by Drown and Martin, and contained a similar proportion of nitrogen (0·05 m.grm. in 10 c.c.).

Sodium Hydroxide free from Ammonium.—100 grms. of caustic soda are dissolved in about a litre of water, boiled down to about half its bulk in an open vessel, then diluted to one litre with water free from ammonium.

Sodium Carbonate free from Ammonium.—200 grms. pure sodium carbonate are dissolved in a litre of water, and the solution boiled briskly until several hundred c.c. have been evaporated.

Determination of Nitrogen Existing as Ammonium.—200 c.c. of the water are placed in a stoppered bottle, 2 c.c. each of the solutions of sodium carbonate and sodium hydroxide added, the stopper inserted, the solutions mixed, and allowed to stand for an hour or two. A filter is prepared by inserting a rather large plug of cotton in a funnel. This should be washed several times with the ammonia-free water. The clear portion of the sample is drawn off with a pipette and run through the filter, the first portions being rejected, since it is diluted by the water retained in the cotton. The filtration is rapid, and when 100 c.c. of the liquid has passed through it is Nesslerised. If the ammonium present is very small in quantity a rather long and narrow tube should be used for observing the colour.

Estimation of Total Organic and Ammoniacal Nitrogen.—500 c.c. of the water are placed in the round-bottomed flask, 10 c.c. of concentrated sulphuric acid added, and the mixture boiled down until the water is driven off and the acid is colourless or pale yellow. The potassium permanganate is then added as above, but after the green colour is obtained the flask is re-heated until the liquid becomes colourless; this requires but a few minutes. After cooling, 50 c.c. of water are added, and then a slight excess of the sodium hydroxide solution; about 150 c.c. will be required. 2 c.c. of sodium carbonate solution are then added to make sure of the precipitation of the calcium and magnesium, though this is perhaps not necessary, since the caustic soda usually contains more than sufficient carbonate for this purpose. The liquid is cooled by immersing the flask in cold water, made up to 250 c.c., transferred to a stoppered bottle, and allowed to stand for about an hour, or until the greater portion of the precipitate has subsided. The clearer portion of the liquid is then drawn off with a pipette and run through the cotton-plug filter described above. The filtrate is perfectly clear and colourless. An aliquot portion is taken and Nesslerised. We prefer to use 100 c.c. and dilute to 200 c.c., using rather larger glasses than are commonly employed. Drown and Martin have noted that the addition of potassium permanganate to the concentrated acid is not essential, and merely employ it as a precautionary measure. With the method detailed above, however, it will be found that unless it is used, the Nesslerised liquid has a yellowish instead of brown colour, and is more difficult to match. A blank experiment is to be made with the reagents used, to determine the amount of the nitrogenous impurity.

We have made trials of the method with various nitrogeneous bodies of known composition, and have invariably obtained the theoretical quantity of nitrogen. As an illustration of the trustworthiness of the method the following is given:—A sample represented to be pure metadiamidobenzene was purified by re-crystallisation, and a solution containing one m.grm.—equivalent to 0·000259 nitrogen—added to 500 c.c. water and treated as above. Only 0·000155 nitrogen was obtained. The experiment was repeated four times with some slight modifications of the process, but with almost precisely the same result. On examination it was found that the material used was in reality metadiamidobenzene dihydrochloride, and contained therefore 0·000154 nitrogen.

The following are a few of the results obtained with natural waters, and a comparison with the results by the distillation method:—

PARTS PER MILLION.

Modified Process.

	Nitrogen.		
	In NH_4.	Organic.	Total.
Water, already impure, to which decomposing urine was added..	0·97	2·34	3·31
Pump-well in densely populated district..	0·24	0·56	0·80
Cellar water—impure	0·17	0·56	0·73

Drown and Martin's Process.

	Nitrogen.			
	In free ammonia.	Organic.	Total.	Lost by boiling.
Water, already impure, to which decomposing urine was added	1·25	1·82	3·07	0·31
Pump-well in densely populated district	0·33	0·38	0·71	0·09
Cellar water—impure ..	0·23	0·41	0·64	0·09

In uncontaminated waters much less difference, and sometimes none, was noticed between the results by the original and the modified process.

The figures show conclusively, we think, even if there were no other observations on the point, that it is not safe to estimate the ammonium in the water by distillation, nor to boil the water previous to the estimation of the organic nitrogen.—*American Chemical Journal*, Vol. xi., No. 4.

NOTICES OF BOOKS.

A Treatise on the Principles of Chemistry. By M. M. PATTISON MUIR, M.A., F.R.S.E., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Second Edition. Cambridge: The University Press.

THE present edition of this work is by no means a mere reprint of its predecessor. The first book has been enriched with the results of researches completed in the meantime; the sections on physical methods have been re-written, the arrangement of several parts has been modified, and chapters which have become of less relative consequence have been shortened. The second book, which has been entirely re-written, discusses the questions of dissociation, chemical change and equilibrium, affinity and the relations between chemical action and distribution of the energy of the changing system. The subject matter of the two books the author summarises respectively as chemical statics and chemical kinetics. Some minds perhaps may better grasp these two phases of the science if they are presented as chemical morphology or the doctrine of structure or composition, and chemical physiology the doctrine of function.

In the first book the author treats of atoms and molecules, of nascent actions, of the dualistic and unitary hypotheses, the equivalence of atoms, of allotropy and isomerism, of molecular compounds, and of the periodic law. A separate section deals with miscellaneous physical methods applicable to questions of chemical statics. It seems to us that the author is now somewhat too ready

to accept the chemical elements as ultimate facts about whose nature and origin it is useless or perhaps unnecessary to enquire. This reminds us of the old school in biology, who quietly accepted every animal and every plant as a *datum* into which it was vain to pry. Now, if we consider the views formerly expressed by Mr. Muir, *e.g.*, in a valuable memoir which he contributed to the *Journal of Science* (1876, p. 30), entitled "Recent Chemical Researches," we should naturally expect from him a thorough and an impartial summary of the evidences for and against the absolute and independent character of our received elements. But this expectation is not gratified. We find, indeed, a full and a fair exposition of the periodic law, but no hint is given as to any light it may throw upon the point at issue. The researches of Mr. Norman Lockyer, in as far as they relate to the decomposition of our conventional simple bodies, are not discussed, nor do the conclusions of the late Sir B. Brodie meet with any appreciation. Assuredly the time is past when the genesis of the elements can be ignored in a work treating on the "Principles of Chemistry." Assuredly, too, there lives no man better able to do justice to this delicate and difficult subject than Mr. Muir.

The second book—"Chemical Kinetics," or, as we should prefer to call it, "Chemical Physiology" (were the term not liable to misunderstanding)—deals with the law of mass-action, with chemical dynamics—a term which some writers use as equivalent to Mr. Muir's "chemical kinetics"—and which includes the velocity of chemical change, chemical equilibrium, the applicability of thermo-dynamical methods to chemical equilibrium (Berthelot's thermo-chemistry), the corresponding application of molecular methods, and dissociation. Then follows the consideration of chemical affinity, including the specific affinity coefficients of acids and bases, the connection between the affinity coefficients, and the constitution of acids. Lastly, the author takes up the subject of chemical change. He concludes with the words:—"Much work has yet to be done before a general theory of chemical change can be hoped for; a theory which shall represent every process of change as a function of the atomic weight of the elements and the affinities of the reacting substances concerned in the operation. When such a theory is attained will chemistry be complete? I hope not; for what's come to perfection perishes."

There is little fear; we must first know what the elements are. Meantime, a thorough study of the work before us will contribute no little to put the advanced student in a position for aiding in perfecting the science.

CORRESPONDENCE.

ALKARSIN.

To the Editor of the Chemical News.

SIR,—The following are equations concerning the alkarsin (arsenide of acetyl) that I discovered. The first has reference to its formation, the second to its decomposition by water, if that take place, and the third to the formation of the alkarsin, acetate of arsenic, if arsenide of acetyl combine with oxygen to form it, which seems highly probable:—

(α). $6C_2H_3OCl + Zn_3As_2 = 2As(C_2H_3O)_3 + 3ZnCl_2$.

(β). $As(C_2H_3O)_3 + 3H_2O = AsH_3 + 3C_2H_4O_2$.

(γ). $As(C_2H_3O)_3 + 3O = As(C_2H_3O_2)_3$.

—I am, &c.,

G. W. BLYTHE, M.P.S.

The Petroleum Association.—Mr. William Fox has been appointed Chemist and Secretary to the Petroleum Association in place of Mr. Boverton Redwood, resigned.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 22, June 3, 1889.

Combustion-heat of Carbon in its Different Conditions as Diamond, Graphite, and Amorphous Carbon.—MM. Berthelot and Petit.—For amorphous carbon the authors obtain the result C_2+O_4: +97·65 calories. Pure crystalline graphite gave for C_2+O_4: + 94·81 cals., whilst the diamond gave 94·31 calories. These values differ from those hitherto accepted based upon the experiments of Favre and Silbermann.

Apparatus for Determining the Melting-point under Ordinary Conditions and at Variable Pressures.—B. C. Damien.—The author's method is chiefly applicable to fatty bodies. The apparatus is a box of 6 c.m. long, 4 c.m. broad, and 3·5 c.m. deep, divided into two distinct compartments, and closed with a lid of gilt brass. Beneath this lid, and touching its side, are two thermometers showing the temperature of the two compartments. The fatty matter, spread out in a thin layer, covers the lid. By means of taps a current of hot water at a temperature a little higher than the approximate melting-point is let pass into the entire box. When the substance is melted cold water is passed into one of the compartments by means of a tube which traverses the apparatus from side to side. At a certain moment the fatty matter is solidified on one side and remains liquid on the other. The observation is easy on account of the different transparency of fats when solid and when melted. The mean of the readings of the two thermometers is the melting-point sought. It is easy to operate at different pressures by substituting two concentric cylinders for the two compartments of the box above described.

The Electric Conductivity of Saline Solutions applied to Chemical Questions. Double Decompositions.—P. Chroustchoff.—The author gives a table of the determinations of the electric conductivity of neutral salts (one equivalent = one litre) capable of undergoing a reaction of double decomposition.

The Electric Conductivity of Saline Solutions containing Mixtures of Neutral Salts.—P. Chroustchoff and V. Pachkoff.—The authors give their results in a tabular form. Their chief object is to furnish experimental evidence in support of the hypothesis that the partial formation of double salts in solutions is a very general phenomenon.

Certain Methods of Producing Mercury-ammonium Chlorides.—G. André.—The author has studied the action of ammonia upon a mixture of mercury chloride and oxide, that of mercury chloride upon a mixture of potassa and ammonia, and that of potassa in excess upon mercury chloramidide in the cold.

The Combinations of Meta-tungstic Acid with the Alkaline and Alkaline-earthy Bases and on the Resulting Thermic Phenomena.—E. Pechard.—The action of an excess of baryta upon metatungstic acid is composed of the following phases:—Formation of barium metatungstate, transformation of the metatungstate into gelatinous neutral tungstate, and transformation of the gelatinous tungstate into a crystalline tungstate, which is the final term of the reaction. This transformation of the metatungstates into the neutral tungstates has been already observed by taking phenolphthalein as indicator, the red colour disappearing as the transformation is effected. This observation, applied to barium, renders it possible to titrate a solution of metatungstic acid. To the acid solution we add a few drops of phenolphthalein

and run in baryta-water as long as the red colour disappears. The baryta-water must then be added, cautiously stirring the liquid and keeping up a gentle heat to promote the formation of the crystalline tungstate. When the last drop has given a permanent red colour four equivalents of baryta have been added for each equivalent of metatungstic acid.

Certain Compounds derived from Ethyl Cyanide by Polymerisation.—M. Hanriot and L. Bouveault.—This paper is not adapted for abstraction.

On the Enrichment of Phosphatic Chalk and on the Origin of the Rich Phosphate of Beauval.—A. Nantier.—By lixiviation a phosphatic mineral can be obtained containing as much as 55 to 60 per cent of actual phosphate. The author supposes that the Beauval mineral, containing 80·9 per cent of pure phosphate, owes its origin to the removal of the calcium carbonate by the action of waters saturated with carbonic acid.

Bulletin de la Société Chimique de Paris.
Vol. i., (Ser. 3), No. 8. April 20, 1889.

The Acetic and Ethylic Ethers of Campho-nitrophenol.—P. Cazeneuve.—An account of campho-nitrophenol acetine and of the ethylic ether of campho-nitrophenol.

The Phosphoric Ether of Campho-nitrophenol.—P. Cazeneuve.—This compound is obtained by boiling campho-nitrophenol for some hours with phosphorus trichloride. It is an amorphous yellowish body, insoluble in water, alcohol, benzene, and most solvents. It is infusible, but it is decomposed by heat and burns with a white flame.

On the Benzoic and Phthalic Ethers of Campho-nitrophenol.—P. Cazeneuve.—The former of these bodies forms small white crystals, insoluble in water, but very soluble in boiling alcohol, ether, and benzene. The phthalic ether forms white crystals, insoluble in water, very slightly soluble in boiling alcohol, insoluble in ether, but more soluble in chloroform and benzene. The crystals melt at 275° with decolouration and slight decomposition.

Researches on the Cadmium Phosphates and Arseniates.—In this paper the author gives an account of the neutral orthophosphate, the mono-cadmium phosphate, the chloro- and bromo-cadmium apatites, the anhydrous cadmium pyrophosphate, and the corresponding arsenical compounds.

The Production of the Neutral Crystalline Lithium Phosphate and of the Corresponding Arseniate.—A. de Schulten.—If lithium chloride is fused with tri-lithium phosphate the latter dissolves easily in the phosphoric acid, its solubility increasing with the temperature. The crystals obtained have the composition Li_3PO_4. They are free from chlorine and form rhomboidal tabular crystals, easily soluble in dilute acids. The corresponding arsenical compound may be obtained in a similar manner.

A Difference of Reaction in Organic Chemistry between the Sulphuric and Selenic Acids.—Prof. Istrati.—Strong sulphuric acid reacts easily upon benzene, its homologues, and their haloid derivatives, yielding a sulphonic derivative, a sulpho-benzide, and a franceine. If selenic is allowed to react upon benzene, neither a franceine nor a selenobenzide is produced.

Transformation of Sulphonic Derivatives under the Influence of Heat in Presence of Sulphuric Acid.—Prof. Istrati.

New Data Concerning the Franceines.—Prof. Istrati.—In one and the same reaction there may be obtained two franceines varying completely in their proportion of chlorine.

On the Franceine derived from $C_6H_3Cl_3$.—Prof. Istrati.—The production of the franceine is directly as the high temperature employed and inversely as the quantity of the sulphonic derivative obtained.

On the Introduction of Acid Radicles into the Molecules of the Acetones.—Dr. L. Claissen.—These two extensive papers do not admit of useful abstraction.

No. 9, May 5, 1889.

Action of Sodium upon Ethyl Cyanide.—M. Hanriot and L. Bouveault.—The authors reject the formulæ proposed by Herr von Meyer in the *Journal für Praktische Chemie*.

Resistance to Light of Colouring-matters when fixed on Tissues.—Jules Joffre.—The author examines the part in the action of light which may be due to oxygen. Chrevreul found, in 1837, that dyed tissues are not discharged if exposed to the action of light in a vacuum, turmeric and prussian blue forming exceptions. The author, in resuming these experiments, placed the dyed swatches, not in a vacuum, but in pure nitrogen gas. Under these a great number of colouring-matters remained unaffected. Among these rank the shades dyed with cyanine which disappear in a few hours' exposure to the sun in the air, but retain all their intensity in the absence of oxygen. The shades obtained with picric acid turn to an orange in nitrogen gas just as in air. The action of atmospheric oxygen may be eliminated by coating the dyed swatches with paraffin or with gum-arabic.

On a Method of Detecting the Presence of Carbon Monoxide in Air.—M. Raceine.—The apparatus which the author has devised is based upon the power of platinum black to absorb carbon monoxide, during which process heat is liberated and an electric current is generated, which rings a bell placed in the circuit.

Transformation of Nitrocamphor into Nitrosocamphor.—P. Cazeneuve.—The author effects this transformation by direct reductive action, heating chloronitrous camphor in dilute alcohol with copper precipitated by zinc.

The Crystallisation of Anhydrous Iodic Acid.—H. Lescœur.—The products obtained on heating nitric and iodic acids together vary with the strength of former acid. With the nitric acid of commerce and with stronger kinds there are obtained flattened crystals formed of trapezoidal plates, which at 170° lose 0·8 per cent of their weight but retain their lustre.

No. 10, May 20, 1889.

Determination of Aniline and of Monomethyl-aniline.—F. Reverdin and Ch. de la Harpe.—The authors weigh out 7 to 8 grms. of the mixture in question and dissolve it in 28 to 32 c.c. of HCl and the quantity of water necessary to make up a total volume of 100 c.c. On the other hand they make up a solution of the "salt R" (a standard solution of the sodium salt of β-naphthol-disulphonic acid) containing, per litre, the quantity corresponding to 10 grms. naphthol. They then measure out 10 c.c. of the solution of the bases and dilute it with a little water and ice and introduce a quantity of sodium nitrite capable of completely diazotising the mixture if it contained nothing but aniline. The product of the reaction is then poured into a measured quantity of the solution of the salt R, to which an excess of sodium carbonate has been added, and proceeding by approximations until, the colouring-matter having been precipitated by sodium chloride, the filtrate no longer gives a red colour on the addition either of the salt R or of diazobenzene chloride. The proportion of aniline contained in the mixture is found from the quantity of the salt R consumed in arriving at this result.

Preparation of Amyl Chloride by Means of Amylic Alcohol.—H. Malbot.—The author saturates the amylic alcohol with hydrochloric acid and heats it in a closed vessel with a considerable proportion of strong hydrochloric acid.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 5 and 6, 1889.

Behaviour of the Mercurous Salts with Ammonia.—C. Barfoed (conclusion).—The author's principal results are:—The ammoniacal precipitates of the mercurous compounds, if exposed to air and placed in circumstances where no chemical decomposition can be assumed, give off about half their mercury in a free gaseous condition, and lose their dark colour. They contain originally equal quantities of free and of combined mercury, but on standing a part of the free mercury enters into combination. The white or pale compounds which remain after the free mercury has evaporated agree with the ammoniacal precipitates of the mercuric salts. The dark precipitates, therefore, are not, as it has been hitherto assumed, ammonium-mercurous compounds, but are mixtures of mercury and ammonium-mercuric compounds. The black precipitate which Kane obtained by an incomplete precipitation of the nitrate with ammonia, and which he regarded as a definite compound, is also a mixture containing mercury. The so-called ammonium mercurous chloride of Rose, obtained from anhydrous ingredients, agrees otherwise with the precipitate of the chloride, but contains also ammonium chloride.

Contributions to the Knowledge of the Polymerisation of the Nitriles (communicated by E. von Meyer).—These contributions include memoirs by R. Holtzwart on di-molecular cyan-methyl; by R. Wache on the polymerisation of certain nitriles; and by E. von Meyer on the chemical constitution of kyanethine, with contributions to a knowledge of its derivatives.

Researches from the Laboratory of the University of Freiburg in Breisgau.—These include memoirs by C. Willgerodt and F. Dürr on our knowledge of solid aceton-chloroform and its derivatives; by C. Willgerodt and A. Kornblum, on the iodation of phenoloid bodies in ammoniacal solution; by K. Elbs and H. Förster on triphenyl trichlorethan and its homologues; by A. Claus and H. Decker on γ-brom-chinolin; and by Ad. Claus on a new dioxynaphthaline.

The Action of Alkalies and Ammonia upon Halogen-substituted Quinones.—Fr. Kehrmann.—A preliminary notice.

Part 7, 1889.

The Determination of Sulphuric Acid in Presence of Iron.—P. Jannasch and Th. W. Richards.—The substance of this paper will be given at some length.

Researches from the Laboratory of Prof. Saytzeff, at Kasan.—We have here papers on the oxidation of erucic acid in an alkaline solution by means of potassium permanganate, by L. Urwanzoff; on the oxidation of ricinoleic acid under similar conditions, by W. Dieff; and a comment on the above papers, by Prof. Saytzeff.

On the Oil of Betel.—J. Bertram and E. Gildemeister.—A study of the essential oil contained in the leaves of the betel (*Piper betle*).

Researches from the Laboratory of the University of Freiburg.—These investigations include a paper by A. Claus and W. Fabrion on carvol and carvacrol-sulphonic acid, and a memoir by A. Claus and A. Dreher on meta-cresol.

On Potassium-Magnesium Bromide.—W. Feit.—This double salt has a composition answering to the formula $KBr,MgBr_2+6H_2O$.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Part ii.

This issue contains no chemical matter.

MISCELLANEOUS.

Elizabeth Thompson Science Fund.—This fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to 25,000 dollars. As accumulated income is again available, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations *which cannot otherwise be provided for*, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed to the solution of questions of merely local importance. Applications for assistance from this fund, in order to receive consideration, must be accompanied by full information, especially in regard to the following points:—(1). Precise amount required. Applicants are reminded that one dollar (1·00 or 1 dollar) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire. (2). Exact nature of the investigation proposed. (3). Conditions under which the research is to be prosecuted. (4). Manner in which the aporopriation asked for is to be expended. All applications should be forwarded to the Secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A. It is intended to make new grants at the end of 1889. The trustees are disinclined for the present to make any grant exceeding five hundred dollars; preference will be given to applications for smaller amounts.

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INDEX.

ARBORESCENT crystals, 37
Abt, W., benzoylen urea, 169
Acetate, benzyl, 301
Acetic sulphide, 240
Acetone, dioxethylic, 72
Acetonic function of nitro-camphor, 97
Acid, boric, 58
carbonic, in air, determination of, 256, 269
dissociation of, 611
chromic, 157
ethers of the camphols, 133
glyceric, preparation of, 93
gymnemic, 159
hydrochloric, new reagent for free, 145
hydrocyanic, 228
mesocamphoric, 277
metaphosphoric, 229
metatungstic, 312
nitric, action of, 92
detection of, 278
in nature, origin of, 144
lecture experiments, 208
naphthalene-sulphonic, 94
of tin, a new, 120
oleic, 168
oxalic, detection of, 206
in the manufacture of aniline, 8
oxalomolybdic, 289
palmitic, sample of, 159
phosphoric, 240
determination, 107
phosphorous, 289
salicylic, determination of, 108
selenic, and other selenium compounds, 219, 232, 258, 267
soils, forage legumens on, 49
sulphonation of naphthalene sulphonic, 60
sulphonic- beta-naphthol, 59
sulphuric, electrolysis of, 133
heat of neutralisation, 237
volumetric estimation of, 58
tartaric, detection, 170
tungstic, separation of stannic oxide from, 73
uric, 240
synthesis of, 279
Acids and metals, interaction of, 202
basicity of, 85
citric and aconitic, 190
isomeric toluric, three, 179
methoxy-naphthalene-sulphonic, 226
tannic and gallic, new tests for, 51
Adie, R. H., compounds of arsenious oxide, 58
Adrian, M., novel sophistication of saffron, 85
Affinity, 221
Agricultural analysis, official methods, 68, 79, 89, 101, 111, 128, 138, 152
"Agricultural Problems of Victoria" (review), 143
"Agriculture, Lectures on" (review), 167
Aikman, C. M., "Basic Slag" (review), 10
Air, determination of carbonic acid and moisture in, 256, 269
expired, poisonous character of, 241
Albumen, determination of, 206
Alcohol, acetopropyl and acetobutyl, 237
assay of, 48, 84
examination of, 121
production of absolute, 181
purification of, 25
Aldehyds, action of, 12
Alkali industry, notes on, 240
in soap, free caustic, 40
Alkalies, action of, 265
Alkaloid, new, 120
Alkaloids, 193
action of, 278
reactions of, 122
Alkarsin, 264, 312
Alla, L., and E. Aubin, determination of organic nitrogen by Kjeldahl's process, 97, 265
Alloys, application of Raoult's depression of melting point to, 175
Alumina, lime, and magnesia, analysis of substances containing, 128
Aluminium, 283
and zirconium, separation of, 100
compounds, a new series, 75, 109
trivalence of, 205
Amat, L., phosphorous acid, 289
"American Pharmaceutical Association, Proceedings" (review), 132
Amide, formation of, 85
Ammonia, behaviour of phenolphthalein with, 214
Ammonium chlorides, reactions of mercury, 97
dithio-carbaminate in analysis, use of, 76
Amorphous bismuth, 107
Amyl chloride, preparation of, 313
Amylodextrin, 295
Anagyrine, 36
Analyses of waters of the Yellowstone National Park, 113, 125, 153, 163
Analysis of butters, &c., 11
Analysis of cinchonas, 196
ethyl fluoride, 11
fertilisers, &c., 7, 19, 31, 42, 53
iron and steel, report of committee on standards, 68
Paris sewage, 193
rain-water, 298
"loss on ignition" in water, 82
official methods of, 68, 79, 89, 101, 111, 128, 138, 152
spectrum, of cadmium, 2, 16, 29
use of potassium manganate in, 301
water, 10, 36
"Ancients, Chemistry of" (review), 192
Anderson, R. J., apparatus to illustrate crystal forms, 203
André, M., reactions of mercury ammonium chlorides, 97, 107, 301, 312
Anhydrous iodic acid, crystallisation, 313
Aniline compounds, 97
determination of, 313
Antimony in minerals, detection of, 15
mordant with whey, 84
Aqueous solutions, rate of chemical change in, 148
Arable and moorland soils, studies, 144
Armstrong, H. E., constitution of betanaphthol-sulphonic acid, 59
interaction of metals and acids, 202
sulphonation of naphthalene sulphonic acid, 60
and E. C. Rossiter, action of halogens on betanaphthol, 225
and W. P. Wynne, constitution of some derivatives of naphthalene, 140, 188
homo- and isomeric hetero-$\alpha\beta$-dichloronaphthalenes, 58
nitration of naphthalene sulphonic acid, 94
Aromatic nitrites, 133
Arsenic in bone-meal, 181
Arsenious oxide, compounds of, 58
Arts, Society of, 25
Ash, indigo stem, 244
"Assayer, the Art of the" (review), 228
Atmosphere, sodium sulphate in, 301
Atomic weight of chromium, 106
of gold, revision, 243
of osmium, 179
of palladium, 262
Atomic weight of ruthenium, 11, 265
of oxygen, 245, 272
of zinc, 297
weights, re-calculations of, 77, 89
Aubin, E., and M. Alla, determination of organic nitrogen by Kjeldahl's process, 97, 265
Auerlite, 67
Aurora spectrum, wave-length of principal line of the, 161
Austen, P. T., "Chemical Lecture Notes" (review), 106
lecture experiments with nitric acid, 208
Australene, researches on, 157
Aylesbury Dairy Co. Laboratory, 84
Aymonnet, M., analysis of Paris sewage, 193
Ayrton, W. E., and J. Perry, electrical measurement, 117
Azo- and diazo-derivatives, 92
Azoles, researches on, 179
Azo-xylenes, 36

BAESSLER, M., manurial value of nitrogen, 84
Bailhache, M., determinations of nitric nitrogen, 293
Barbier, P., and J. Hilt, researches on australene, 157
Barfoed, C., behaviour of mercurous salts, 314
Barium sodium hyposulphate, 133
sulphate, reduction to sulphide, 309
Barth, M., peats of Alsace-Loraine, 144
"Basic Slag" (review), 10
Baubigny, H., action of sulphuretted hydrogen, 53
separation of zinc and cobalt, 149
and nickel, 88
Baumann, A., origin of nitric and nitrous acid in nature, 144
Beam, W., and H. Leffmann, estimation of nitrogen in water, 310
"Examination of Water" (review), 252
Beaurepaire, N., formation of durol, 37
Beer analysis, 152
Benedikt, R., and M. Cantor, determination of glycerin, 108
E. Ehrdich, and F. Ulzer, gum lac, 160
Benzene derivatives, 157
vapour in gas, 37

Benzidine, ether of, 206
Benzol-phenol, homologues of, 185, 195, 215
Benzo leu-urea, 169
Benzyl acetate, 301
Beringer, C., and J. J., volumetric determination of sulphur, 41
Berthelot, M., action of acids on the hyposulphites, 277
alkalies, 265
oxygenated water, 48
benzene vapour in gas, 37
fixation of nitrogen, 167, 217
origin of bronze, 265
oxygenated water and chromic acid, 157
reactions of hydrogen peroxide, 97
and M. Petit, combustion-heat of carbon, 312
"Introduction to the Study of the Chemistry of the Ancients" (review), 192
Besana, C., butter, 85
Bevan, E. J., and C. F. Cross, chemistry of the flax fibre, 135
of lignification, 106
Bidet, A., derivatives of benzene, 157
Bidwell, S., two lecture experiments, 203
Biquartz, use of, 300
Bismuth, amorphous, 107
electric resistance of, 301
Bismuthous oxide, cubical form of, 57
Blake, J., molecular properties and action of inorganic compounds, 60
Blood, detection of, 47
quantity of water in, 300
Blount, B., separation of silica and sand, 277
solubility of brass, 47
Blowpipe analysis, 47
"Blowpipe in Chemistry, &c." (review), 35
Blue, Egyptian or Vestorian, 119
Prussian, new solvents for, 97
Blum, L., analysis of substances containing alumina, lime, and magnesia, 128
Blyth, A. W., and G. H. Robertson, experiments on butter-fat, 58
Blythe, G. W., acetic sulphide, 240
alkarsin, 264, 312
hydrocyanic acid, 228
Boas, Dr., new reagent for free hydrochloric acid, 145
Boiler incrustations, formation of marine, 222, 234
Boilers, examination of feed-water for steam, 207
Bone-meal, arsenic in, 181
Bonz, A., formation of amides, 85
"Books, Catalogue of Second-hand and New" (review), 10
Borax, action of, 277
manufacture of, 108
Boric acid, 58
Bornträger, H., examination of alcohol, 121
Bouchardat, G., and J. Lafont, conversion of terpilene into a menthene, 72, 120
Boulger, G. S., "Uses of Plants" (review), 300
Bourquelot, E., saccharine, 254
sugars of certain fungi, 168
Bouty, E., electrolysis of sulphuric acid, 133
Boys, C. V., quartz as an insulator, 203
Bradbury, C. M., true formula for permanganates, 115, 123, 136, 149
Braithwaite, J., "Retrospect of Medicine" (review), 71
Braive, E., grisoutite, 169
Brass, solubility of, 47, 119
Brauner, B., nickel and cobalt, 72
Brauner, B., researches on the periodic law, 295
Brazier, Professor (obituary), 46
Bréal, E., detection of nitric acid, 278
Brignone, M., determination of chlorides in urine, 109
'British Journal Photographic Almanack" (review), 24
Bromine, iodine, &c., detection of, 281
Bronze, origin of, 265
Brown, H. T., and G. H. Morris, amylodextrin, 295
Brullé, R., determination of sulphur in coal, 108
Burchard, O., oxidation of hydrogen iodide, 73
Burmese petroleum, 292
Business, bad manners in, 109
Butter, 85
fat experiments, 58
influence of diet on the melting point of, 121
Butters, &c., analysis of, 11
Butylic ethers, 97

CACAO starch, 193
Cadmium phosphates, 313
spectrum, analysis of, 2, 16, 29
Caffeine, synthesis of, 305
Cameron, C. A., and J. Macallan, selenic acid and other selenium compounds, 219, 232, 258, 267
Camphols, acid ethers of the, 133
Campho-nitrophenates, 240
Cantor, M., and R. Benedikt, determination of glycerin, 108
Caoutchouc in plants, 109
Carbohydrates, molecular weights of, 296
Carbon, combustion-heat of, 312
disulphide, decomposition of, 140
in steel, estimating, 158
monoxide, detection, 120, 313
fatal poisoning by, 260
Carbonic acid, dissociation of, 61
in air, determination of, 256, 269
Carles, P., gold arseniate, 254
Carnegie, D. J., cupric iodide, 57
Carnelley, T., "Heating and Ventilation of Schools" (review), 142
Carnot, A., cobalt and nickel peroxides, 183
new method of determining lithia, 171
separation of cobalt and nickel, 208
use of hydrogen peroxide, 15, 48
Castelhaz, J., manganese oxalate, 36
Castor oil, 180
Catlett, C., and F. W. Clarke, platiniferous nickel ore from Canada, 294
Causse, H., action of the aldehyds, 12
determination of sugar, 36
Caustic alkalies, examination of flesh for, 206
Caustic alkali of soap, 280
Cazeneuve, P., acetonic function of nitro-camphor, 97
campho-nitrophenates, 240
nitrophenol, isomeric, 107
transformation of nitrocamphor into nitrosocamphor, 230, 313
and L. Hugounenq, homopterocarpine, 36
Central Institution, Exhibition Road, 37
Charpentier, P., error in the assay of fine gold, 179
Chassy, A., electric transfer of dissolved salts, 179
Chauvin, H., researches with Iceland spar, 301
Chemical change in aqueous solutions, rate of, 148
Chemical compounds, voltaic energy of dissolved, 159
electro-studies, 61
Institute of the University of Strassburg, 133
laboratory at Sydney, proposed, 23
at Zurich, 179
of Prof. Saytzeff at Kasan, 169
of Wiesbaden, 145
problem, a, 143
society, 57, 92, 104, 140, 156, 174, 188, 200, 224, 236, 247, 295
president's address, 200
"Chemical and Physical Apparatus and Chemicals Catalogue" (review), 119
"Chemical Lecture Notes" (review), 106
Chemistry of lignification, 106
of the flax fibre, 135
organic, difference of reaction in, 313
Sexton's inorganic, 48, 72
"Chemistry, Elementary Inorganic" (review), 71, 72
"Chemistry, Elementary, Textbook of" (review), 300
"Chemistry, The Blowpipe in" (review), 35
"Chemistry of Chlorophyll" (review), 287
"Chemistry of the Ancients, Study of" (review), 192
"Chemistry of Photography" (review), 191
"Chemistry, Practical Organic" (review), 178
"Chemistry, Principles of" (review), 311
"Chemistry, Treatise on" (review), 217
Chenevier, A., oxidation of linseed oil, 12
Chevreul, Prof. (obituary), 179
Chlorate, potassium, decomposition of, 63
Chloride of amyl, preparation, 313
platinic, 277
Chlorides, determination of, 109
Chlorine, bromine, iodine, detection of, 281
development of, 205
gas, preparation of, 230
Chloroform, action on phenylhydrazin, 141
Chlorophyll, colouring-matter of, 278
"Chlorophyll, Chemistry of" (review), 287
Christy, T., "New Commercial Plants and Drugs" (review), 228
Chromic oxide, detections of, 109
Chromium, atomic weight of, 106
manganese, &c., separation of iron from, 232
Chromium, preparation of the oxy-haloid derivatives, 184
Chroustchoff, P., electro-conductivity of saline solutions, 301, 312
Cinchonas, analysis of, 196
Citric and aconitic acids, 190
City and Guilds of London Institute, 37
Clark cell, 166
Clarke, F. W., "Table of Specific Gravities" (review), 252
and C. Catlett, platiniferous nickel ore from Canada, 294
Clay, W. F., "Catalogue of Standard Second-hand and New Books" (review), 10
Coal, determination of sulphur in, 108
measures, some new fossil resins from the, 1
Cobalt and nickel, decomposition of, 29, 39, 64, 72, 149
peroxides, 183, 205
separation of, 208
solution for depositing metallic, 64
to iron, relation of, 93
volumetric estimation of, 51
Coke ash as manure, 241
Collie, N., note on methyl fluoride, 94
some compounds of tribenzylphosphine oxide, 176
some leadhills minerals, 156
Colman, H. G., and W. H. Perkin, Jun., acetopropyl and acetobutyl alcohol, 237
Colouring-matters on tissues, resistance to light, 313
Colson, A., colouring-matters from the tetrabenzylic ether of benzidine, 206
diquinolic base, 11
on a diquinolic base, 120
researches on the alkaloids, 193
Combes, A. and C., syntheses of hydropyridic bases, 72
trivalence of aluminium, 205
Combustion-tubes, apparatus for drying, 308
Copper and nitric acid, reactions between, 303
influence of on the determination of iron, 207
salts, reaction of, 168
reduction of, 85
separation from lead, cadmium, &c., 222
"Cosmic Evolution" (review), 177
Cotton-seed oil and beef-fat in lard, 99
Cotton tissues, bleaching, 157
Croll, J., "Stellar Evolution" (review), 253
Crookes, W., W. Odling, and C. M. Tidy, London water supply, 91, 138, 196, 246, 310
Cross, C. F., and E. J. Bevan, chemistry of lignification, 106
of the flax fibre, 135
Cryolite, 180
Crystal forms, apparatus to illustrate, 203
structures, formation of a cross in certain, 117
Cundill, J. P., "Dictionary of Explosives" (review), 263
Cundall, T. J., a zinc mineral from a blast furnace, 202
Cupric iodide, 57
Cuprous chloride, preparation of, 168
Curci, A., action of earthy-alkaline metals, 289
Cyanethine, chemical constitution of, 169
$C_{21}Cl_{36}$ compounds, 262

DAMIEN, B. C., apparatus for determining the melting point, 312
D'Arcy, R. F., a compound of boric acid with sulphuric anhydride, 58
Davis, J. T., separation of aluminium and zirconium, 100
De Boisbaudran, L., gadolinium of M. de Marignac, 97
De Chardonnet, M., artificial silk, 265
De Clermont, P., danger of using white lead in lace, 206
use of saccharine, 199
De Coninck, O., ptomaines, 230
study of the ptomaines, 48
De Koninck, L. L., determination of manganese, 230
preparation of chlorine gas, 230
removal of fused masses from platinum crucibles, 121
De Marignac, the gadolinium of, 97
De Mondesir, P., forage legumens on acid soils, 49
lime combined in soils, 97
De Schulten, A., neutral crystalline lithium phosphate, 313
De Wilde, P, and A. Reychler, transformation of oleic acid into stearic acid, 168
De la Harpe, C., and F. Reverdin, determination of aniline, &c., 313

De la Harpe, C., and F. Reverdin, determination of nitrotoluene, 12
Des Cloiseaux, M., a new mineral, 60
Dehérain, P. P., losses and gains of nitrogen in field experiments, 254
Delachanal, M., and C. Vincent. extraction of sorbite, 72
sorbite, 120
Delacharlonny, P. M., suppression of the potato disease, 254
and L. Destremx, ferrous sulphate, 84
Delezinier, A. M., a new ptomaine, 120
Delmart, A., and Ebell, P., use of oxygenated water for bleaching wool, wood, &c., 84
Delta-metal, 108
report on the alloy known as, 230
Demski, H., and Morawski, T., determination of resin oils in mineral oils, 206
Denigès, G., preparation of cuprous chloride, 168
reagents for the mercaptan function, 119
thiophene, 169
Destremx, L., and P. M. Delacharlonny, ferrous sulphate, 84
Diacetyl, 305
pentane and dibenzoyl-pentane, 237
Diamagnetic bodies, impossibility of, 288
Diamine compounds, metallic, 98
Diastase, saccharification by, 144
Dichloronaphthalenes, homo- and isomeric hetero-$\alpha\beta$, 58
Dioxethylic acetone, 72
Diquinolic base, 11, 120
Disinfectant, new, 291
Dixon, A. E., improved apparatus for use in drying combustion tubes, 308
isothiocyanites, 176
H. B., and H. W. Smith, incompleteness of combustion in gaseous explosions, 65
Donath, E., and R. Jeller, detection of chromic oxide, 109
and F. Müllner, separation of stannic oxide from tungstic acid, 73
Dressing, resistance to the bleaching processes, 25
Drouin, R., succinnamic nitrile, 198
Drown, T. M., "loss on ignition" in water analysis, 82
and H. Martin, determination of nitrogen by Kjeldahl method, 272
"Drugs and Plants, New Commercial" (review), 228
Duhem, P., impossibility of diamagnetic bodies, 288
Dunnington, F. P., use of hydrogen peroxide in analysis, 76
Dunstan, W. R., skatole in the vegetable kingdom, 291
Durol, formation of, 37

EBELL, P., and A. Delmart, use of oxygenated water for bleaching wool, &c., 84
Eber, W., reactions of eserine, 206
Edmunds, L., "Patents, Designs, and Trade Marks Acts" (review), 251
Edwards, V., estimation of insoluble phosphates, 159
Egger, E., application of Pettenkofer's bile-acid reaction, 169
Eggertz, C. G., studies on arable and moorland soils, 144
Egyptian or Vestorian blue, 119
Ehrdich, E., R. Benedikt, and F. Ulzer, gum lac, 180
Eidam, E., adulteration of linseed meal, 144
Eissler, M., "Metallurgy of Gold" (review), 253
Electric conductivity of melted salts, 72
current, oxidations by means of, 293
radiation, concentration of, 250
resistance of bismuth, 301
transfer of dissolved salts, 179
sugar, 24, 35
Electrical measurement, 117
resistance, 117
Electricity, voltaic effect on germination, 174
Electro-chemical studies, 61
Electro-conductivity of saline solutions, 301, 312
"Electro-deposition" (review), 204
Electro-magnetic units, dimension of, 118
Electro-magnets, suppressing sparking in, 299
Electrolysis, initial phase of, 179
of sulphuric acid, 133
Electrolytes, dissociation theory of, 61
loss of voltaic energy of, 183
Electrolytic conductivity, application of, 180
Electrostatic field produced by varying magnetic induction, 250
Embroidery, report on process for colouring metals for, 230
Ergot of rye, new proximate principle in, 144
Ericaceæ on calcareous soils, 278
Ernde, B., detection of iron in Turkey-red oils, 84
Eserine, reactions of, 206
Ethers, butylic, 97
hydrochloric, preparation of, 218
Ethyl fluoride, analysis of, 11
Explosives, improvements in the manufacture of, 25
"Explosives, Dictionary of (review), 263
"Explosives, Report of Inspectors" (review), 227
Explosive substances, new, 157

FABER, H., variations in the composition of milk, 253
Faraday lecture, 241
Farsky, M., peat, 84
Ferro-manganese with low percentage of carbon, 75
Ferrous sulphate, 84, 96, 106, 229
Fertilisers, analysis of, 7, 19, 31, 42, 53
Fish guano, experiments, 240
Fitzgerald, G. S., dimension of electro-magnetic units, 118
Flax fibre, chemistry of the, 135
Flückiger, M., coloured reactions of strychnine, 121
Fluoride, methyl and isobutyl, 48
thiophosphoryl, 236
Fluorides, preparation of propyl and isopropyl, 120
Fluorine in the organism, 241
Foerster, M. O., determination of oil of mustard, 85
Formic acid, preparation of concentrated, 37
Fouqué, F., Egyptian or Vestorian blue, 119
Fragner, C., new alkaloid, 120
Franceine, 313
new, 36
Frank, M., detection of nitrates in soils, 240
Freiburg University, laboratory of, 314
Fresenius, H., arsenic in bone-meal, 181
Friedel, C., mesocamphoric acid, 277
Fumigator, automatic, 280

GADOLINIUM of M. de Marignac, 97
Gallic and tannic acids, new tests for, 52
Gallon, N., and E. Hardy, anagyrine, 36
Gas chlorine, preparation of, 230
cylinder, note on the explosion of, 75, 96
nitrogen, method of preparing, 135, 171
presence of benzene vapour in, 37
"Gas Works Statistics" (review), 288
Gases, law of the solubility of, 193
Gaseous explosions, incompleteness of combustion in, 65
Gatellier, E., and L. L'Hote, richness of wheat in gluten, 277
Gautier, A., and L. Hallopeau, certain new metallic sulphides, 229, 301
Gelis, E., and A. Riche, "The Art of the Assayer" (review), 228
Genvresse, M., experiments of, 120
Geometrical optics, 299
Georgesco and Mincou, MM., new franceine, 36
Ghilian, A, volumetric method of determining manganese, 121
Girard, C., and L. L'Hote, compounds of aniline, 97
and A. Müntz, production of farm-yard manure, 265
and X. Rocques, assay of alcohol, 48, 84
H., methyl-acetanilide, 218
Gladstone, J. H., and W. Hibbert, atomic weight of zinc, 297
Glaze for bricks, white, 145
Gleditsch, A., and H. Moeller, three isomeric toluric acids, 179
Glyceric acid, preparation of, 93
Glycerin, determination of, 108
estimation of, 134, 170
Gold arseniate, 254
atomic weight of, 243
error in the assay of, 179
"Gold, Metallurgy of" (review), 253
Goniometer, refraction, 203
Gooch, F. A., and J. E. Whitfield, analyses of waters of the Yellowstone National Park, 113, 125, 153, 163
Gore, G., determining the strength of liquids, 243
loss of voltaic energy of electrolytes during chemical union, 183
rate of chemical change in aqueous solutions, 148
voltaic energy of dissolved chemical compounds, 159
Gorgen, A., action of air on manganese carbonate, 277
manganese oxides, 265
Granval and Valser, MM., commercial oleic acid, 145
Graphites, physical properties of, 29
Gréhant and Quinquaud, MM., quantity of water in blood, 300
Green, A. G., constitution of primuline and allied sulphur compounds, 177
Griffiths, A. B., "Treatise on Manures" (review), 191
Grimaux, E., and L. Lefèvre, dioxethylic acetone, 72
Grimbert, L., and E. Jungfleisch, inverted sugar, 72
Grisoutite, 169
Grünwald, A., spectrum analysis of cadmium, 2, 16, 29
Grüssner, A., and K. Hazura, castor oil, 180
Gunning, J., modification of the Kjeldahl process, 241
Gum-lac, 180
Guinti, M., error in determination of nitrates in soils, 254
Guttmann, O., improvements in the manufacture of explosives, 25
Gymnemic acid, 159

HABERMANN, J., production of absolute alcohol on the small scale, 181
Haldane, J. S., and M. S. Pembrey, determination of carbonic acid and moisture in air, 256, 269
Haller, A., acid ethers of the camphols, 133
phthalates, 144
Hallopeau, L., and A. Gautier, certain new metallic sulphides, 229, 301
Halogens, action of the, 40
on beta-naphthol, action, 225
Hambly, F. J., and T. E. Thorpe, vapour density of hydrogen fluoride, 104
Hansen, A., signification of the colouring matter of chlorophyll, 278
Harcourt, A. V., "Pentane Standard and Pentane Lamps" (review), 288
Hardy, E., and N. Gallon, anagyrine, 36
Hartley, W. N., note on the explosion of a gas cylinder, 75
Hautefeuille and Perrey, MM., reproduction of zircons, 11
Hawkridge, P., volumetric composition of nitrogen oxides, 66
Hazura, K., and A. Grüssner, castor oil, 180
Hegler, J., reproduction products of hematoxyline, 13
Hematoxyline, 13
Heptine of perseite, 60
Hérard, F., amorphous bismuth, 107
Herschel, A. S., physico-geometrical models, 96
Heycock, C. T., and E. H. Neville, application of Raoult's depression of melting point to alloys, 175
Hibbert, W., and J. H. Gladstone, atomic weight of zinc, 297
Hidden, W. E., and J. B. Mackintosh, new thorium mineral, auerlite, 67
Hilt, J., and P. Barbier, researches on australene, 157
Hiorns, A. H., "Text-book of Elementary Metallurgy" (review), 34
Hirsch, R., oxalic acid as a by-product of the manufacture of aniline, 84
Hodgkinson, W. R., blowpipe analysis, 47
and F. K. S. Lowndes, decomposition of potassium chlorate, 63
Hoff, J. H., and L. T. Reicher, dissociation theory of the electrolytes, 61
Hoffert, M., photograph of lightning flashes, 299
Hogg, T. W., determination of iron in ferro-alloys, 207
Holland, P., estimation of titanium, 27
Homopterocarpine, 36
Hooper, D., gymnemic acid, 159
Horn, F. M., determination of paraffin, 108
Horses, rational feeding of, 266
Hospital, London, 301
"Household lye," substitute for soap and soda, 108
Howard, J. L., and O. J. Lodge, concentration of electric radiation, 250
Hüfner, G., absorptive power of grey vulcanised rubber, 181
Huggins, W., wave length of principal line of the spectrum of the aurora, 161

Hugounenq, L., and P. Cazeneuve, homopterocarpine, 36
Humin compounds, 240
Hunt, L. G., and C. S. S. Webster, action of the halogens,
Hurst, G. H., notes on ochres, siennas, and umbers, 172
Hutchinson, A., and M. M. P. Muir, cubical form of bismuthous oxide, 57
Hydrochloric acid, determination of, 145
new reagent for free, 145
ethers, preparation of, 218
Hydrocyanic acid, 228
Hydrogen fluoride, vapour density, 104
iodide, oxidation of, 73
peroxide, reactions of, 97
use of, 15, 35, 48, 76
sulphuretted, action of, 53
Hypophosphorous acid, action of, 36
Hydropyridic bases, syntheses of, 72
Hyposulphites, action of acids on, 277

ICE, influence of pressure on the volatilising point of, 231
Iceland spar, researches with, 301
Ince, W. H., formation of phenylindoles, 249
Indian ink, 47
Indican, detection of, 206
Indigo stem ash, 244
Industrial Society of Mulhouse, 25, 108
Inorganic chemistry, Sexton's, 48, 72
compounds, molecular properties and action of, 60
Institution, Royal, 71, 118, 166, 181, 227, 239, 241
"Internal Revenue, Report of Commissioner for the Fiscal Year ending June 30, 1888" (review), 132
Iodic acid, anhydrous crystallisation, 313
Iodide, cupric, 57
oxidation of hydrogen, 73
Iodoform, preparation of, 72
Iron and steel ships, corrosion and fouling, 197, 210
standards for the analysis of, 68
detection of, 84
in ferro-alloys, determination of, 207
in minerals, detecting minute quantities, 231
separation from chromium, manganese, &c., 232
sulphur in determination of, 107
Iron to cobalt, relation of, 93
Isobutyl and methyl fluorides, 48
Isomeric toluric acids, three, 179
Isothiocyanites, 176
Istrati, M., difference of reaction in organic chemistry, 313

JANSSEN, J., terrestrial origin of the oxygen rays in the solar spectrum, 281
Jaksch, A., signal lights for ships and lighthouses, 118
Jeller, R., and E. Donath, detection of chromic oxide, 109
Jensen, J. L., researches on smut, mildew, and canker in grain, 84
Joffre, J., resistance to light of colouring-matters on tissues, 313
Johnson, G. S., atomic weight of oxygen, 272
solubility of white precipitate, 234
Johnstone, A., detecting minute quantities of iron in minerals, 231
detection of mercury in minerals, 221
Johnstone, A., rapid and sure detection of antimony in minerals, 15
Jolles, A., use of potassium manganate in analysis, 301
Joly, A., atomic weight of ruthenium, 11, 265
nitroso-compounds of ruthenium, 230
Jones, A., determination of stannous salts, 84
Jones, J. V., use of Lissajou's figures, 165
Jorgensen, S. M., metallic diamine compounds, 98
Jungfleisch, E., and L. Grimbert, inverted sugar, 72
and E. Lèger, oxycinchonine, 265

KASAN, laboratory of Prof. Saytzeff, 314
Kassner, G., determination of caoutchouc in plants, 109
Kayser, E., mercury in commercial tin, 84
Keiser, E. H., atomic weight of palladium, 262
Keller, H. F., diacetyl and some of its derivatives, 305
and E. F. Smith, on the compound $C_{21}Cl_{20}$, 262
Kern, S., ferro-manganese with low percentage of carbon, 75
Kestner, M. S., notes on the alkali industry, 240
Keyworth, G. A., electric sugar, 24
Kilogramme, alloy of standard, 254
Kimmins, C. W., periodates, 57
Kipping, F. S., and W. H. Perkin, Jun., diacetyl-pentane and dibenzoyl-pentane, 237
Kirkland, J. B., and O. Masson, salts of triethylsulphine, &c., 95
Kjeldahl's method for the determination of organic nitrogen, 97, 272, 310
process, modification of, 241, 265
Klein, J., use of ammonium dithiocarbaminate in analysis, 76
Knapp, F., ultramarine by the moist way, 12
Kœchlin, C., resistance of dressing to the bleaching processes, 25
Kraut, K., barium sodium hyposulphate, 133
Kreusler, M., detection of nitrates in the soil, 144
Kretzschmar, M., preservation of wood, 180
abridged method for determining potassium in ashes, &c., 109
antimony mordant with whey, 84
Krüss, G., and F. W. Schmidt, researches on cobalt and nickel, 64
Kühn, J., ericaceæ on calcareous soils, 278

LACE, danger of using white lead in, 206
Lachowitz, B., acid character of the salts of the heavy metals, 169
Lafont, J., and G. Bouchardat, conversion of terpilene into a menthene, 72, 120
Lalande, M., assay of smoking opium, 205
Lamal, A., aqueous solutions of the morphine salts, 120
Lambert, A., action of borax, 277
Lange, J., and J. Lunge, water-gas, 180
Landrin, E., analysis of cinchonas, 196
Lard, cotton-seed oil and beef-fat in, 90
Le Chatelier, H., solubility of salts, 229
dissociation of carbonic acid, 61
expansion of metals at high temperatures, 301
Lead and tin, determination of an alloy of, 72
cadmium, &c., separation of copper from, 222
determination, 73
Leadhills minerals, 156
Leaper, C. J., fatal explosion of a gas cylinder at Dublin, 96
Lecerf, C., determination of albumen, 206
Lefèvre, L., and E. Grimaux, dioxethylic acetone, 72
Leffmann, H., and W. Beam, estimation of nitrogen in water, 310
"Examination of Water" (review), 252
Leger, E., dangers from tin covers containing lead, 254
and E. Jungfleisch, oxycinchonine, 265
Leidie, E., rhodium, 57
Leonard, N., colouration of a coal fire by common salt, 15
Lescœur, H., crystallisation of anhydrous iodic acid, 313
Lewes, V. B., corrosion and fouling of steel and iron ships, 197, 210
formation of marine boiler incrustations, 222, 234
Lewkowitsch, J., improved Soxhlet extractor and vacuum distilling apparatus, 249
sawarri fat, 225
preparation of glyceric acid, 93
L'Hote, L., determination of organic nitrogen, 48, 230
and E. Gatellier, richness of wheat in gluten, 277
and C. Girard, compounds of aniline, 97
Lightning flashes, photograph of, 299
Light, polarised, three notes on, 70, 276
resistance to of colouring-matters on tissues, 313
Lignification, chemistry of, 106
Lime combined in soils, 97
Lime, magnesia, and alumina, analysis of substances containing, 128
Lindet, L., maltose, 240
saccharification by diastase, 144
Ling, A. R., derivatives of halogen nitrophenols, 156
Linseed meal, adulteration of, 144
oil, oxidation of, 12
Lippmann, G., obtaining photographs in accurate values, 254
Liquids, determining the strength, 243
viscous, 266
Lissajou's figures, use of, 165
Lithia, new method of determining, 171
Lithium phosphate, neutral crystalline, 313
Lloyd R., homologues of benzolphenol, 185, 195, 215
Lodge, O., electrostatic field produced by varying magnetic induction, 250
magneto-optic rotation by transient currents, 141
and J. L. Howard, concentration of electric radiation, 250
"Logic, Empirical or Inductive" (review), 204
Logwood extracts, testing, 262
London Hospital, 301
University, 193
water supply, 91, 138, 196, 246, 310
Long, J. H., behaviour of phenolphalein with ammonia, 214
Lownes, F. K. S., and W. R. Hodgkinson, decomposition of potassium chlorate, 63
Lunge, J., and J. Lange, water-gas, 180
Lupke, R., signification of potash in the plant, 240

MACADAM, W. I., some new fossil resins from the coal measures, 1
Macallan, J., and C. A. Cameron, selenic acid and other selenium compounds, 219, 232, 258, 267
Mackintosh, J. B., and W. E. Hidden, new thorium mineral, auerlite, 67
Magnetic induction, electrostatic field produced by, 250
viscosity, 124
Magneto-optic rotation, 141
Malbot, H., preparation of amyl chloride, 313
preparation of hydrochloric ethers, 218
Mallet, J. W., revision of the atomic weight of gold, 243
Maltose, 240
Manganese carbonate, action of air, 277
chromium, separation of iron from, 232
determination of, 230
oxalate, 36
oxides, 265
volumetric method of determining, 121
Mannite, 133
Manure, coke ash as, 241
farmyard, formation of, 218, 229, 265
Manures, treatise on, 145
"Manures, Treatise on" (review), 191
Manurial experiments, 254
Maquenne, M., heptine of perseite, 60
preparation of concentrated formic acid, 37
Marcacci, A., action of the alkaloids on plants and animals, 278
Marcano, V., alcoholic fermentation of the juice of the sugar-cane, 265
and A. Müntz, formation of nitre earths, 253
nitrates in rain-water of tropical regions, 289
Marine boiler incrustations formation of, 222, 234
Marsh, C. W., detection of chlorine, bromine, iodine &c., 281
reduction of barium sulphate to sulphide, 309
Martin, H., and T. M. Drown, determination of nitrogen by Kjeldahl method, 272
Marx, L., yeasts of wines, 25
Mason, W. P., detection of blood, 47
fatal poisoning by carbon monoxide, 260
Mason, G., "Pictures in Black and White" (review), 10
Masson, O., and J. B. Kirkland, salts of trieth, lsulphine, &c., 95
Mayer, A., influence of diet on the melting point of butter, 121
McCulloch, N., estimation of cobalt and nickel, 205
use of peroxide of hydrogen, 35
volumetric estimation of cobalt, 51
McIntosh, J. G., action of ferrous sulphate on soils, 96, 167, 229
Medicine, Academy of, 11
"Medicine, Retrospect of" (review), 71
Meinecke, C., determination of sulphur in iron, 107
studies on siderurgy, 121
Meissl, E., result of manurial experiments, 254
Meldola, R., "Chemistry of Photography" (review), 191
and G. T. Morgan, constitution of azo- and diazo-derivatives, 92

Meisens, M., preparation of propyl and isopropyl fluorides, 120
Mercaptan function, reagents for, 119
Mercurous salts, behaviour of, 314
Mercury ammonium chlorides, 97, 107, 165, 301, 312
cyanide, action of, 11
detection of, 221
in commercial tin, 84
and tin, separation, 193
Meslans, H., and H. Moissan, methyl and isobutyl fluoride, 48
Mesocamphoric acid, 277
Metallic cobalt, solution for depositing, 64
diamine compounds, 98
sulphides, certain new, 229, 301
"Metallurgy, Text-book of Elementary" (review), 34
Metals, acid character of the heavy, 169
action of earthy alkaline, 289
and acids, interaction, 202
at high temperatures, expansion, 301
in acids, rate of dissolution of, 202
molecular weights of, 174
new, 234
Metaphosphoric acid, 229
Methyl acetanilide, 218
fluoride, 94
Melting-point, apparatus for determining, 312
Meunier, J., mannite, 133
Meyer's, V., modification of vapour-density method, 39
Milk, alcoholic fermentation of, 289
analysis, 7
variations in the composition, 253
"Milk and Vinegar, Report of Inspector" (review), 264
Mincou, M., and M. Georgesco, on a new franceine, 36
Mineral, a new, 60
zinc, from a blast-furnace, 202
Minerals, detection of antimony in, 15
of minute quantities of iron, 231
solubility of different in sea-water, 218
some leadhills, 156
Mittelbach, F., uric acid, 240
Mixter, W. G., "Elementary Text-book of Chemistry" (review), 300
Moeller, H., and A. Gleditsch, three isomeric toluric acids, 179
Moissan, H., analysis of ethyl fluoride, 11
and H. Meslans, methyl and isobutyl fluoride, 48
Monnet, L., reduction of copper salts, 85
Monoxide, carbon, detection of, 120
Moore, T., volumetric estimation of nickel, 160, 292
Morawski, T., and H. Demski, determination of resin oils in mineral oils, 206
detection of resin, 193
Morgan, G. T., and K. Meldola, constitution of azo- and diazo-derivatives, 92
Morphine salts, aqueous solutions of, 120
Morris, G. H., action of sulphur on resin, 298
and H. T. Brown, amylodextrin, 295
Muir, M. M. P., and A. Hutchinson, cubical form of bismuthous oxide, 57
"Treatise on the Principles of Chemistry" (review), 311
Mulhouse, Industrial Society of, 25, 108
Müllner, F., and E. Donath, separation of stannic oxide from tungstic acid, 73
Müntz, A., and C. Girard, production of farmyard manure, 265
and V. Marcano, formation of nitre earths, 253
nitrates in rain-water of tropical regions, 289
fertilising properties of the waters of the Nile, 157
Museum, Parkes, 241
Mustard oil, determination of, 85

NANTIER, A., enrichment of phosphatic chalk, 313
Naphtha, 218
Naphthalene, some derivatives of, 140, 188
sulphonic acid, nitration of, 94
sulphonation of, 60
Neumann, G., determination of zinc, 180
Neville, E. H., and C. T. Heycock, application of Raoult's depression of melting-point to alloys, 175
Newlands, electric sugar, 35
Nickel and cobalt, decomposition, 29, 39, 64, 72, 149
peroxides, 183, 205
separation of, 208
and zinc, separation of, 88
ore, platiniferous, from Canada, 294
volumetric estimation, 160, 292
Nitrates, error in the determination, 254
in rain-water of tropical regions, 289
in the soil, detection, 144, 240
Nitre earth, formation of, 253
Nitric acid, action of, 92
and copper, reactions between, 303
detection of, 278
in nature, origin, 144
lecture experiments with, 208
nitrogen, determination of, 293
oxide, certain compounds of, 277
Nitrites, aromatic, 133
Nitriles, polymerisation of, 314
succinamic, 193
Nitro-camphor, acetonic function of, 97
transformation into nitroso-camphor, 230, 313
Nitrophenol, isomeric, 107
Nitrophenols, derivatives of, halogen, 156
Nitrotoluene, determination of, 12
Nitroso-compounds of ruthenium, 230
Nitrogen compounds, magnetic, rotation of, 247
determination of, 45, 272, 310
by various methods, 230
organic, 48
fixation of, 167, 217
gas, method of preparing, 135, 171
losses and gains in field experiments, 254
loss of gaseous during decomposition of organic matter, 107, 109
manurial value of, 84
organic determination of, 97
oxides, volumetric composition of, 66
source of error in determining, 181
Noelting, E., and B. Strecker, azoxylenes, 36
North, B., volumetric estimation of sulphuric acid, 58
Noyes, W. A., atomic weight of oxygen, 245

OBITUARY:—Dr. Isidor Soyka, 133
John Williams, 118
Prof. Brazier, 46
Prof. Chevreul, 179
Robert Romanis, 251
Ochres, siennas, and umbers, notes on, 172
Odling, W., W. Crookes, and C. M. Tidy, London water supply, 91, 138, 196, 246, 310
Oil, castor, 180
cotton-seed, and beef fat in lard, 99
linseed, oxidation of, 12
of mustard, determination of, 85
walnut, 279
Oils, non-siccative, 180
tests for essential, 25
Oleic acid, commercial, 145
Olive oil, falsification of, 230
Opium, smoking, assay of, 205
"Organic Chemistry, Practical" (review), 178
Organic compounds, combustion heat of some, 301
matter, loss of gaseous nitrogen during decomposition, 107, 109
matters, slow combustion of certain, 157
nitrogen, determination of, 97
Osman, W., jun., and W. J. Russell, relation of cobalt to iron, 93
Osmium, atomic weight, 179
Ossipoff, J., combustion heat of some organic compounds, 301
experiments of M. Genvresse, 120
Ostwald, W., determination of the basicity of acids, 85
electro-chemical studies, 61
Oxalate, manganese, 36
Oxalic acid, detection of, 206
in the manufacture of aniline, 84
Oxalomolybdic acid, 289
Oxidations by means of the electric current, 293
Oxide, detection of chromic, 109
tribenzyl phosphine, some compounds of, 176
Oxides of manganese, 265
nitrogen, volumetric composition of, 66
Oxycinchonine, 265
Oxygen, atomic weight of, 245, 272
rays of solar spectrum, origin of, 281
separation from the atmosphere, 99
Oxy-haloid derivatives of chromium, preparation of, 184

PAGNOUL, A., analysis of wine, 205
Paint, iron oxide, 134, 145
Palladium, atomic weight of, 262
Palmer, T. C., testing logwood extracts, 262
Palmitic acid, sample of, 159
Paper and inks, report on safety, 230
Paraffin, determination of, 108
Paragalactine, 277
Paris, plaster of, 61, 74
Parkes museum, 241
Parmentier, F., sodium sulphate in the atmosphere, 301
Passerini, R., ash of coke as manure, 241
Patent laws, 109
"Patents, Designs, and Trade Marks Act" (review), 251
Pearson, A. M., "Some Agricultural Problems of Victoria" (review), 143
Peat, 84
Peats of Alsace-Loraine, 144
Péchard, A., oxalomolybdic acid, 289
metatungstic acid, 312
Pembrey, M. S., and J. S. Haldane, determination of carbonic acid and moisture in air, 256, 269
"Pentane Standard and Pentane Lamps" (review), 288
Percival, J., methoxynaphthalene sulphonic acids, 226
Periodates, 57
Periodic law, researches on, 295
Perkin, A. G., action of nitric acid on anthracene, 92
W. H., magnetic rotation of nitrogen compounds, 247
W. H., jun., and H. G. Colman, acetopropyl and acetobutyl alcohol, 237
and F. S. Kipping, diacetylpentane and dibenzoyl-pentane, 237
Perman, E. P., boiling point of sodium and potassium, 237
Permanganates, true formula for, 115, 123, 136, 149
Peroxide of hydrogen, use of, 15, 35, 48, 76
cobalt and nickel, 183, 205
Perrey and Hautefeuille, MM., reproduction of zircons, 11
Perry, J., and Ayrton, W. E., electrical measurement, 117
Petermann, M., phosphoric acid 240
Petit and Berthélot, MM., combustion heat of carbon, 312
Petroleum Association, 312
Burmese, 292
Pettenkofer's bile-acid reaction, application of 169
"Pharmaceutical Association, Proceedings of the American" (review), 132
Pharmaceutical Society, 289
"Pharmacy, Introductory Address at the Albany College" (review), 35
"Pharmacy, Year Book of" (review), 71
Phenolphthalein with ammonia, behaviour of, 214
Phenol, reddening of, 181
Phenylindoles, formation of, 249
Phenylnaphthalene, note on, 225
Phillips, S. E., notes on recent and future research, 160
synthesis of caffeine, 305
of uric acid, 279
Phipson, T. L., presence of tin in certain kinds of sugar, 255
Phosphate, neutral crystalline lithium, 313
Phosphates, action of various, 45
estimation of insoluble, 159
of cadmium, 313
"Phosphates, Our Supply of" (review), 24
Phosphatic chalk, enrichment of, 313
Phosphoric acid, 240
determination of, 107
Phosphorous acid, 289
Photograph of lightning flashes, 299
Photographs of accurate values obtaining, 254
Photographic map of the normal solar spectrum, 124
Photography, use of sodium sulphite, 157
"Photography, Chemistry of" (review), 191
"Photography, Dictionary of" (review), 132
Phthalates, 144
"Physical and Chemical Apparatus, Catalogue" (review), 119
Physical Society, 70, 96, 117, 141, 165, 203, 249, 276, 299
Physico-geometrical models, 96
Pickering, S. U., expansion of water, &c., 249
heat of neutralisation of sulphuric acid, 237
nature of solutions, 248
solubility of brass, 119
"Pictures in Black and White" (review), 10
Piffard, B., Indian ink, 47
Pigeon, L., platinic chloride, 277
Piltschinoff, M., initial phase of electrolysis, 179
Planchon, V., analysis of butters &c., 11
Plants, caoutchouc in, 109
"Plants, Uses of" (review), 300

Plaster of Paris, 61, 74
Platinic chloride, 277
Platiniferous nickel ore from Canada, 294
Platinum crucibles, removal of fused masses from, 121
Poincaré, L., electric conductivity of melted salts, 72
Poire, P., use of sodium sulphite in photography, 157
Polarimeter, new, 117
Pollen, resistance of, 278
Pollock, A., and R. Threlfall, Clark cell, 166
Potash in the plant, signification of, 240
Potassic chlorate, decomposition of, 104
Potassium and sodium, boiling point of, 237
chlorate, decomposition of, 63
determination of, 109
manganate in analysis, use of, 301
Potato disease, suppression, 254
starch, transformation of, 241
Primuline and allied sulphur compounds, constitution, 177
Propyl and isopropyl fluorides, preparation, 120
Prost, E., and W. Spring, development of chlorine, 205
Ptomaine, a new, 120
Ptomaines, 230
and their genesis, 2
study of the, 48
Pulfrich, C., new refractometer, 181

QUANTIN, H., volumetric determination of sulphates, 73
Quartz as an insulator, 203
Quinquaud and Gréhant, MM., quantity of water in blood, 300

RACEINE, M., detecting carbon monoxide in air, 313
Rain-water, analysis of, 298
of tropical regions, nitrates in, 289
Ramsay, W., molecular weights of the metals, 174
Raoult's depression of melting point to alloys, application of, 175
Raulin, J., action of various phosphates, 45
Rawson, S. G., atomic weight of chromium, 106
attempts to prepare the oxyhaloid derivatives of chromium, 184
new tests for tannic and gallic acids, 52
Rayleigh, Lord, composition of water, 147
Raynaud, H., and H. Suilliot, preparation of iodoform, 72
Reboul, E., butylic ethers, 97
Reboux, E., purification of alcohol, 25
Refractometer, new, 181
Reicher, L. T., and J. H. Hoff, dissociation theory of the electrolytes, 61
Reichardt, E., disposal of refuse by irrigation or removal, 265
Reichert, E., application of electrolytic conductivity, 180
Reiset, J., formation of farmyard manure, 218, 229
Renault, L., detection of indican, 206
Research, notes on recent and future, 160
Resin, action of sulphur on, 298
detection of, 193
oils, determination of, 206
Resins, fossil, some new from the coal measures, 1
Reverdin, F., and C. de la Harpe, determination of aniline, &c., 313
determination of nitrotoluene, 12
Reychler, A., and P. De Wilde, transformation of oleic acid into stearic acid, 168
Reynolds, E. J., a new disinfectant, thiocamf, 291
silicon compounds, 296
Rhodium, 37
Richards, T. W., method of vapour density determination, 87
modification of Victor Meyer's vapour density method, 39
Riche, A., and E. Gelis, "The Art of the Assayer" (review), 228
Rideal, S., "Practical Organic Chemistry" (review), 178
Ridsdale, E. A., "Cosmic Evolution" (review), 177
Rittinghaus, P., resistance of pollen, 278
Robertson, G. H., and A. W. Blyth, experiments on butter fat, 58.
Rocques, X., and C. Girard, assay of alcohol, 48, 84
Rodger, J. W., and T. E. Thorpe, thiophosphoryl fluoride. 236
Roe, W., sheep dressing, 179
Romanis, R., Burmese petroleum, 292
(obituary), 251
Roscoe, H. E., aluminium, 283
and C. Schorlemmer, "Treatise on Chemistry" (review), 217
Ross, W. A., "The Blowpipe in Chemistry, &c." (review), 35
Rossiter, E. C., and H. E. Armstrong, action of halogens on betanaphthol, 225
Roth, M., manurial experiments, 254
Rowland, H. A., photographic map of the normal solar spectrum, 124
Royal Institution, 71, 118, 166, 181, 227, 239, 241
society, 238
Rubber, absorptive power of grey vulcanised, 181
Ruhemann, S., action of chloroform and alcoholic potash on phenylhydrazine, 141
and S. Skinner, citric and aconitic acids, 190
Russell, W. J., and W. Orsman, jun., relation of cobalt to iron, 93
Ruthenium, atomic weight of, 11, 265
nitroso-compounds of, 230
Rye, ergot of, new proximate principle in, 60, 144

SABATIER, P., transformation of metaphosphoric acid, 229
Saccharine, use of, 199, 254
Saffron, novel sophistication of, 85
Salicylic acid, determination of, 108
Salt, common, colouration of a coal fire by, 15
Salts of copper, reaction, 168
reduction of, 85
aqueous solutions of the morphine, 120
mercurous, behaviour of, 314
solubility of, 229
Saltsien, P., cacao starch, 193
Salzer, M., detection of tartaric acid, 170
Sanitary Institute, 37
Sawarri fat, 225
Saytzeff, Prof., chemical laboratory, 169, 314
Scheurer, A., bleaching cotton tissues, 157
Schloesing, T., loss of gaseous nitrogen during decomposition of organic matter, 107, 109
Schloesing, T., jun., slow combustion of certain organic matters, 157
Schmidt, F. W., and G. Krüss, cobalt and nickel, 64
"Schools, Heating and Ventilation of" (review), 142
Schorlemmer, C., and H. E. Roscoe, "Treatise on Chemistry" (review), 217
Schulze, E., paragalactine, 277
Schunck, E., "Chemistry of Chlorophyll" (review), 287
Science and Art Department, 13 26, 36
fund, Elizabeth Thompson, 314
Sea-water, solubility of different minerals in, 218
Seelig, E., benzyl acetate, 301
Selenic acid and other selenium compounds, 219, 232, 258, 267
"Sell's Dictionary of the World's Press" (review), 71
Seubert, K., atomic weight of osmium, 179
Sewage, analysis of, 193
utilisation, 144
Sexton, A. H., "Elementary Inorganic Chemistry" (review), 71
Sexton's inorganic chemistry, 48, 72
Seyler, F. H., humin compounds, 240
Sheep dressing, 179
Ships and lighthouses, signal lights, 118
steel and iron, corrosion and fouling, 197, 210
Shunt transformer, 299
Siderurgy, studies on, 121
Siennas, ochres, and umbers, notes on, 172
Silica and sand, separation of, 277
Silicon compounds, 296
Silk, artificial, 265
"Silver Ores, Lixiviation of with Hyposulphite Solutions" (review), 178
Sjögvist, J., determination of hydrochloric acid, 145
Skatole in the vegetable kingdom, 291
Skinner, S., and S. Ruhemann, citric and aconitic acids, 190
"Slag, Basic" (review), 10
Smith, E. F., oxidations by means of the electric current, 293
and H. F. Keller, on the compound $C_{21}Cl_{28}$, 262
Smith, E. W., shunt transformer, 299
Smith, H. W., and H. B. Dixon, incompleteness of combustion in gaseous explosions, 65
Smith, W., note on phenylnaphthalene, 225
Smut, mildew, &c., researches, 84
Snowdon, R., a chemical problem, 143
Soap, free caustic alkali in, 40, 280
Society, Chemical, 57, 92, 104, 140, 156, 174, 188, 200, 224, 236, 247, 295
president's address, 200
of Arts, 25
of Mulhouse, Industrial, 25, 108
Pharmaceutical, 289
Physical, 70, 96, 117, 141, 165, 203, 249, 276, 299
Royal, 238
Sodium and potassium, boiling-point of, 237
sulphate in the atmosphere, 301
hyposulphate, barium, 133
Soils, lime combined in, 97
studies of arable and moorland, 144
Solar spectrum, origin of the oxygen rays in, 281
photographic map of the normal, 124
Solom, 73
Solutions, nature of, 248
Sorbite, 120
Sorbite, extraction of, 72
Soxhlet, extractor, improved, 249
Soyka, Dr. Isidor (obituary), 133
Specific resistances, high, 166
"Specific Gravities, Table" (review), 252
Spectrum analysis of cadmium, 2, 16, 29
of the aurora, wave-length of principal line of the, 161
Spirituous liquors, examination, 180
Spring, W., a new acid of tin, 120
and E. Prost, development of chlorine, 205
Stannic oxide, 289
separation from tungstic acid, 73
Stannous salts, determination, 84
Starch, transformation of potato, 241
Stearic acid, 168
Steel and iron ships, corrosion and fouling of, 197, 210
standards for the analysis of, 68
dishes, enamelled, 220
Steiger, E., paragalactine, 277
"Stellar Evolution" (review), 253
Stettefeldt, C. A., "Lixiviation of Silver Ores with Hyposulphite Solutions" (review), 178
Strecker, B., and E. Noelting, azoxylenes, 36
Strychnine, coloured reactions of, 121
Succinamic nitrile, 193
Sugar-cane, alcoholic fermentation of the juice of, 265
Sugar, determination of, 36
in cereals, 180
inverted, 72
presence of tin in certain kinds of, 255
Sugars of certain fungi, 168
Suilliot, H., and H. Raynaud, preparation of iodoform, 72
Sulphate, action of ferrous on soils, 167, 192, 229
of lime, 85
Sulphates, volumetric determination of, 73
Sulphide, acetic, 240
Sulphides, certain metallic, 301
metallic, 229
Sulphonic acid, betanaphthol, 59
Sulphur compounds, constitution of primuline and allied, 177
in coal, determination of, 108
in iron, determination of, 107
on resin, action of, 298
volumetric determination of, 41
Sulphuretted hydrogen, action of, 53
Sulphuric acid, electrolysis of, 133
heat of neutralisation of, 237
in the air, 229
volumetric estimation, 58
Sydney University, proposed chemical laboratory at, 23

TAMMAN, G., fluorine in the organism, 241
Tannic and gallic acids, new tests for, 52
Tannin, determination of, 193
Tanret, C., new proximate principle in the ergot of rye, 60
Tartaric acid, detection of, 170
Taylor, T. J., "British Journal Photographic Almanack" (review), 24
Tea tannin, estimation, 261
Tellurium, 295
Terpilene, conversion into a menthene, 72, 120
Thiophene, 169
Thiophosphoryl fluoride, 236
Thiocamf, a new disinfectant, 291
Thompson, Elizabeth, Science fund, 314

Thompson, Prof., formation of a cross in certain crystal structures, 117
Thompson, S. P., geometrical optics, 299
new polarimeter, 117
polarised light, 70, 276
suppressing sparking in electro-magnets, 299
Thorium mineral, new, 67
Thorpe, T. E., decompoision of carbon disulphide by shock, 140
Thorpe, T. E., and F. J. Hambly, vapour-density of hydrogen fluoride, 104
Thorpe, T. E., and J. W. Rodger, thiophosphoryl fluoride, 236
Thoulet, J., solubility of different minerals in sea-water, 218
Threlfall, R., and A. Pollock, Clark cell, 166
Tichborne, C. R. C., best method of preparing nitrogen, 171
Tidy, C. M., W. Crookes, and W. Odling, London water supply, 91, 138, 196, 246, 310
Tin and lead, determination of an allov of, 72
and mercury, separation of, 193
a new acid of, 120
covers containing lead, dangers from, 254
in certain kinds of sugar, 255
mercury in, 84
oxidability and cleansing, 60
Titanium, estimation of, 27
"Trade-marks, Patents, and Designs Acts" (review), 251
Traube, J., examination of spirituous liquors, 180
Tribenzylphosphine oxide, some compounds of, 176
Triethylsulphine salts, 95
Trotter, A. P., refraction goniometer. 203
Tucker, W. G., "Introductory Address at the Albany College of Pharmacy" (review), 35
Tuson, the late Professor, 13

UCUHUBA, the fat of, 180
Ultramarine by the moist way, 12
Ulzer, F., R. Benedikt, and E. Ehrdich, gum lac, 180
Umbers, ochres, and siennas, notes on, 172
University of Freiburg, laboratory, 314
of London, 193
of Strassburg, chemical institute of the, 133
Urea in blood and in the muscles, 300
Uric acid, 240
synthesis of, 279

VACUUM distilling apparatus, 249
Valenta, E., the fat of ucuhuba, 180
Valser, M., and M. Granval, commercial oleic acid, 145
Van Aubel, E., electric resistance of bismuth, 301
Vapour-density determination, method, 87
method, modification of, 39
pressures, 298
Varet, R., action of mercury cyanide, 11
Veley, V. H. rate of dissolution of metals in acids, 202
reactions between copper and nitric acid, 303
Venable, F. P., re-calculations of the atomic weights, 77, 89
Venn, J., "Principles of Empirical or Inductive Logic" (review), 204
Vieth, P., Aylesbury Dairy Co., 84
Vignon, L., oxidability and the cleansing of tin, 60
stannic oxide, 289
water analysis, 36
Ville, J., action of hypophosphorous acid, 36
Ville, M. G., "Lectures on Agriculture" (review), 167
Vincent, M., and M. Delachanal, sorbite, 72, 120
"Vinegar and Milk, Report of Inspector" (review), 264
Violle, J., alloy of the standard kilogramme, 254
Violette, C., determination of organic nitrogen, 97
Vitali, D., examination of flesh for caustic alkalies, 206
Volumetric estimation of cobalt, 51
of nickel, 292
Von Asboth, A., presence of sugar in cereals, 180
Von Knorre, G., separation of copper from lead, cadmium, &c., 222
of iron from chromium, manganese, &c., 232
Von Lippmann, E., paragalactine, 277
Von Meyer, E., chemical constitution of cyanethine, 169
Von Reiss, M. A., determinatio of phosphoric acid, 107
Voss, H., "Our Suppl · of Phosphates" (review), 24

WAGHORNE, J. W., elec trical resistance, 117
Wall, E. J., "Dictionary of Photography" (review), 132
Walnut oil, 279
Wanklyn, J. A., water analysis, 10
"Water Analysis" (review), 46
Ward, A. W., use of biquartz, 300
Warren, H. N., affinity, 221
automatic fumigator, 280
effects of voltaic electricity towards germination, 174
method of preparing nitrogen gas, 135
partial separation of oxygen from the atmosphere, 99
physical properties of graphites, 29
solution for depositing metallic cobalt, 64
Warren, T. T. P. B., contamination of water with lead, 256
examination of feed-water for steam boilers, 207
magnetic viscosity, 124
oxygenated, and chromic acid, 157
for bleaching wool, 84
supply of London, 91, 138, 196, 246, 310
"Water Analysis" (review), 46
"Water, Examination of" (review), 252
"Water Works Statistics" (review), 288
Waters, analyses of the Yellowstone National Park, 113, 125, 153, 163
of the Nile, fertilising properties of, 157
Webster, C. S. S., and L. G. Hunt, action of the halogens, 40
Weight, molecular, 266
Weights, molecular, of the metals, 174
Wheat, richness of in gluten, 277
Whey, antimony mordant with, 84
White, J. T., estimation of tea tannin, 261
indigo stem ash, 244
White precipitate, solubility of, 234
Whitfield, J. E., and F. A. Gooch analyses of waters the Yellowstone National Park, 113, 125, 153, 163
Wiesbaden, chemical laboratory of, 145
Williams, John, obituary, 118
Wilm, T., separation of tin and mercury, 193
Wilson, J. A., determination of free caustic alkali in soap, 40
cotton-seed oil and beef fat in lard, 99
free caustic alkali of soap, 280
note on a sediment deposited from a mixture used in calico printing, 221
J. C. A., sample of palmitic acid, 159
Wines, analysis of, 138, 205
Wines, yeasts of, 25
Wislicenus, Prof., communications from the laboratory of, 133
Witting, F., manufacture of borax, 108
Woukoloff, M., law of the solubility of gases, 193
Wood preservation, 180
Wool, bleaching, 84
Würtz, R., poisonous character of air expired, 241
Wyborn, J. M., ptomaines and their genesis, 2
Wynne, W. P., and H. E. Armstrong, constitution of some derivatives of naphthalene 140, 188
homo- and isomeric hetero-αβ-dichloronaphthalenes, 58
nitration of naphthalene sulphonic acid, 94

YEAST of wines, 25
Youle, W. E., Science and Art Department, 36
Young, S., influence of pressure on the volatilising point of ice, &c., 231
vapour pressures, 298
Yvon, M., volumetric determination of lead, 73

ZECHNISSEN, H., transformation of potato starch, 241
Zinc and nickel, separation of, 88
atomic weight of, 297
determination of, 180
mineral from a blast furnace, 202
Zircons, reproduction of, 11
Zirconium and aluminium, separation of, 100
Zsigmondy, R., cryolite, 180
source of error in determining the nitrogen of halogeniferous bodies, 181

END OF VOLUME LIX.

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CONTAINING

INDEX AND TITLE-PAGE TO VOLUME LX.

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VOLUME LX.—1889.

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LONDON:

PRINTED BY EDWIN JOHN DAVEY.

BOY COURT, LUDGATE HILL, E.C.

THE CHEMICAL NEWS.

VOLUME LX.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1545.—JULY 5, 1889.

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.*

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk-Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen, and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully dried powders of potash saltpetre and acetate of soda in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—nitrate of soda and acetate of potash.

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars; for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun nitrogen surrounded by its planets of hydrogen, and common salt (NaCl) may be looked upon as a double star formed of nitrogen and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrate visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor is capable of being destroyed. Therefore, in chemistry we must seek dynamic equilibrium, not only between the molecules, but also in their midst among their competent atoms. Many conditions of such equilibrium have been determined, but much remains to be done; and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of death-like inactivity.

* A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order was for a long time hid from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every subdivision from the largest masses to the smallest particles, and consequently their characteristics must be a property of its particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it; so much so, that the astrologers imagined a connection between the individualities of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learnt to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary bodies, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry because the soil is only being now prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oyxgen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches of chemists. They have sought everywhere, and have always found systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There, where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those which are diametrically opposite; yet among these, dynamical equilibrium establishes itself, not only by excluding one or other of the forces, but regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts, and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and on the other, the disintegration or scattering of the new particles formed, as well as of those originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions: according to the one, solution seems a mere act of building up or association; according to the other, it is only dissociation or disintegration. The truth lies evidently between these views; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon; and consequently the sympathies and antipathies, which it was thought to transfer from human relations to those of atoms, should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed or, as it were, dissolved by carbon, which leads us to suspect incipient chemical action, even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove, and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Ste. Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and applied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, "affinity." Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules; in one word, the vast mass of the most

important chemical researches of the present day, clearly indicates the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the Principia of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal-tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not, on the face of it, directly applicable to the investigation of other elements, because, in examining the first, it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, while in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, while the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements, such, for example, as their ability to enter into various combinations, and their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But, by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements "under given conditions"; and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomers possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, while the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term "structural" is so appropriate to the contemporary views of the above order, and that the "constructors" seek to justify the tetrahedric, plane, or prismatic disposition of the atoms of carbon in benzole. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chess board: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy, which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat only a small portion of it, namely, of *substitutions*, without specially considering combinations and decompositions, and, even then, limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_4 or CH_6 as the remnants of molecules CH_4 or C_2H_6 we shall not pause to consider them, because, as far as we know, they fall asunder into two parts, H_2+H_2 or CH_4+H_2, as soon as they are even temporarily formed, and are capable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond to elements the atomic weight of which decrease consecutively,

$$F = 19,\ O = 16,\ N = 14,\ C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base upon which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate, that is of combining with water; and the similar attribute of ammonia, resulting in the formation of a caustic alkali, NH_3H_2O, or NH_4OH.

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure, or rather construction of molecules, that is to say, their constitution and transformations, without having recourse to the teaching of "structionists," but on Newton's dynamical principles.

Of Newton's three laws of motion, only the third can be applied directly to chemical molecules when regarded

as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which, the mass of evidence collected in modern times, forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton's third law, which is applicable to every system, declares that, "action is always associated with reaction, and is equal to it." The brevity and conciseness of this axiom was, however, qualified by Newton in a more expanded statement, "the action of bodies one upon another is always equal, and in opposite directions." This simple fact constitutes the point of departure for explaining dynamic equilibrium, that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structionists express by atomicity or the valency of the elements, and, in connection with them, the various numbers of affinities. In reality if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word, every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom "the principle of substitution," and let us apply it to those typical forms of hydrogen compounds, which we have already discussed, and which, on account of their simplicity and regularity, have served as starting points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example the molecules of chlorine, Cl_2, and of hydrogen, H_2, and hydrochloric acid HCl, which is familiar to all in aqueous solution as spirit of salt, and which has many points of resemblance with HF, HB_2, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner, this same principle of substitution was exhibited. Chlorine and bromine acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen —reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalies, constituted similarly to water, and even on water itself—only, however, under the influence of light, and only partially because of the unstability of HClO—forms by this principle bleaching salts, which are the same as the alkalies, but with their hydrogen replaced by chlorine. In ammonia and in methane, chlorine can also replace the hydrogen. From ammonia is formed in this manner the so-called chloride of nitrogen, NCl_3, which decomposes very readily with violent explosion on account of the evolved gases, and falls asunder as chlorine and nitrogen. Out of marsh gas, or methane, CH_4, may be obtained consecutively, by this method, every possible substitution, of which chloroform, $CHCl_3$, is the best known, and chloro-carbonic acid, CCl_4, the most instructive. But by virtue of the fact that chlorine and bromine act, in the manner shown, on the simplest typical hydrogen compounds, their action on the more complicated ones may be assumed to be the same. This can be easily demonstrated. The hydrogen of benzole, C_6H_6, reacts feebly under the influence of light on liquid bromine, but Gustavson has shown that the addition of the smallest quantity of metallic aluminium causes energetic action, and the evolution of large volumes of bromide of hydrogen.

If we pass on to the second typical hydrogen compound, that is to say water, its molecule, HOH, may be split up in two ways: either into an atom of hydrogen and a molecule of oxide of hydrogen, HO, or into oxygen, O, and two atoms of hydrogen, H; and therefore, according to the principle of substitution, it is evident that one atom of hydrogen can exchange with oxide of hydrogen, HO, and two atoms of hydrogen, H, with one atom of oxygen, O.

Both these forms of substitution will constitute methods of oxidation, that is to say, of the entrance of oxygen into the compound—a reaction which is so common in nature as well as in the arts, taking place at the expense of the oxygen of the air or by the aid of various oxidising substances or bodies which part easily with their oxygen. There is no occasion to reckon up the unlimited number of cases of such oxidising reactions. It is sufficient to state that in the first of these oxygen is directly transferred, and the position, the chemical function, which hydrogen originally occupied is, after the substitution, occupied by the hydroxyl. Thus ammonia, NH_3, yields, hydroxylamine, $NH_2(OH)$, a substance which retains many of the properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitution of the hydrogen by its oxide, methylic, $CH_3(OH)$, and other alcohols. The substitution of one atom of oxygen for two atoms of hydrogen is equally common with hydrogen compounds. By this means alcoholic liquids containing ethyl alcohol, or spirits of wine, $C_2H_5(OH)$, are oxidised till they become vinegar or acetic acid, $C_2H_3O(OH)$. In the same way caustic ammonia, or the combination of ammonia with water, NH_3H_2O, or $NH_4(OH)$, which contains a great deal of hydrogen, by oxidation exchanges four atoms of hydrogen for two atoms of oxygen, and become converted into nitric acid, $NO_2(OH)$. This process of conversion of ammonia salts into saltpetre goes on in the fields every summer, and with especial rapidity in tropical countries. The method by which this is accomplished, though complex, though involving the agency of all-permeating micro-organisms, is, in the substance, the same as that by which alcohol is converted into acetic acid, or glycol, $C_2H_4(OH)_2$, into oxalic acid, if we view the process of oxidation in the light of the Newtonian principles.

(To be continued).

A VOLUMETRIC METHOD FOR THE ESTIMATION OF FAT IN MILK.

By G. E. PATRICK.

A METHOD which I have recently devised for the rapid estimation of fat in milk, consists in bringing all the milk solids, excepting fat, into acid solution in a solvent which is without sensible action upon the fat, and then measuring the latter at a fixed temperature in a narrow calibrated tube.

The solvent which I use is a mixture of strong acetic acid (80 per cent or upwards in strength), oil of vitriol, and concentrated hydrochloric acid, in about the proportions of 9, 5, and 2 by volume. The HCl is added after the mixture of the other two is cooled. These proportions may be varied considerably without much impairing the efficiency of the solvent. Thus, mixtures of 9, 4, and 4 volumes respectively, and even of 9, 3, and 3, have given good results; but the first-mentioned mixture effects solution quicker, gives fully as clear a solution, and, I have frequently thought, leaves less fat adhering to the walls of the tube as it (the fat) subsides to its place for measurement. Even a mixture of acetic and hydrochloric or of acetic and sulphuric, in the proportions of 9 to 5 or 6 by volume, does fairly well, but neither is as satisfactory as a mixture of the three.

It also seems worth recording that any material increase in the amount of HCl in the various mixtures named results in more or less turbidity of the milk solution, and thereby renders somewhat difficult the accurate reading of the fat. If from any cause this turbidity ever appears it can be avoided in a second trial by simply increasing the proportion of acetic acid, making a mixture of about 11, 5, and 2 volumes respectively. The increase of acetic acid retards somewhat the solvent action, while giving a lighter coloured and clearer solution of the milk solids.

The proportion of the solvent to the milk analysed may also be varied considerably without affecting the final results. I take usually 10·8 c.c. milk and 15 c.c. of the solvent. The operation is performed in a tube about 30 c.m. long, of about 17 m.m. calibre, excepting for a distance of 7 or 8 c.m. near the middle, where it is reduced to a thick-walled tube of about 5 m.m. calibre. The low part or body of the tube holds 21 to 22 c.c., and when charged the liquid fills the narrow portion and reaches about 2 c.m. above it. By means of a lateral perforation in the body of the tube, kept closed by a rubber band (a section of tubing) also perforated, the latter perforation being a little to one side of the former, using a pin as a lever, the liquid may be gradually withdrawn, and the fat made to enter the narrow part, which is graduated in divisions of 0·025 c.c. each. If 10·8 c.c. of milk are taken one such division = 0·2 per cent of fat, measured at 60° C., assuming average densities for both milk and fat. Of course any other scale and any other charge of milk may be employed, provided the tube be correctly proportioned. Before charging the tube there are placed in its lower part (best enclosed there when the tube is made) two pieces of pumice stone joined together by a bit of platinum wire, a very effective combination proposed by Dr. G. C. Caldwell, to promote the regular boiling of liquids. In charging the tube the milk is first pipetted in, half or more of the required acid mixture is then added and well shaken with it, and the remainder then poured in—or a quantity sufficient to bring the liquid to the proper height in the tube. The charged tube is placed on a sand-bath, its contents heated to boiling, boiled quite briskly for ten minutes, then rather gently for ten minutes, or longer if necessary, in order to collect the fat in a layer at the top, and keep it gently agitated with an up-and-down motion until perfectly clear. A little practice is required to learn how best to manage the heat in this latter stage of boiling. When the fat layer is perfectly clear the tube is immediately placed in water at 60° C. for ten minutes, and if great accuracy is not required the fat is at once lowered into the graduated tube, and its volume read at 60° after re-immersion in the water for a few moments. In the descent a little fat usually adheres to the tube, making the reading low by 0·05 to 0·2 per cent. Therefore, for exact results, the column of fat is only lowered until its top is just above that of the graduated tube; with a few drops of ether the adhering fat is washed down, the tube is replaced in hot water until the ether is *entirely* expelled, after which the fat is lowered and read at 60° C.

Results agree well with those by the Adams process as modified by Thompson* (filter-paper instead of blotting-paper), seldom differing from them by more than 0·1 per cent on samples of mixed milk.

The process has not yet been tested on milk from individual cows, all tests thus far having been on the mixed milk from a herd of thirty.

The process is very expeditious; with a little practice one can make three or four determinations, side by side, in an hour and a half.

Agricultural Experiment Station, Ames, Iowa,
June 13, 1889.

THE ACTION OF SILICON ON THE METALS GOLD, SILVER, PLATINUM, AND MERCURY.

By H. N. WARREN, Research Analyst.

WITH regard to the action of silicon on the more common metals, iron and copper, so well known are the properties in general of these elements when combined, that little, if any, comment is required; but on passing to the more refractory metals a much wider field for study is presented.

As recorded by the various handbooks of chemistry, silicon, when in the nascent state, converts platinum into a brittle silicide. This is by no means, however, the only method available for preparing this compound; for, on heating graphitoidal silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus, being fusible at a red heat, and breaking with a crystalline fracture, at the same time being difficultly soluble in acids. The same compound may be more readily formed by heating in a closed crucible a mixture of amorphous silicon and platinum black under a layer of potassium silico-fluoride, the analysis of several results thus obtained proved the presence of 10 per cent silicon. On the other hand, neither silver or gold present any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride, metallic sodium, and either silver or gold in the amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance, the alloy, containing as little as 5 per cent silicon, is almost as brittle as antimony, and, to all appearances, resembles gold alloyed with a due proportion of silver. At the same time, although silicon possesses no considerable affinity towards either gold or silver, except when in a nascent state, still that affinity appears to be considerably enhanced by combining with either metal, when in the fused condition, a small quantity of an already prepared silicide of either gold, silver, or platinum. Thus, if on to the surface of a quantity of either silver or gold in the fused condition is ejected a few grains of an already prepared silicide of either gold or silver, complete mixture of the same at once ensues. This alloy, although containing but a minute percentage of silicon, may be raised to a much higher rate by the introduction of elementary silicon, which, before this period, showed at all normal temperatures no great affinity, except when in a nascent form;

* *Analyst*, 1886, p. 73.

silver when thus impregnated with from 10 per cent of silicon, becomes of a slightly red tint, resembling in appearance metallic manganese. The regulus, after being pulverised, being completely decomposed by the aid of concentrated hydriodic acid.

As regards the action of silicon on metallic mercury nothing very definite can at present be stated, but on subjecting a small vessel containing mercury in contact with an alcoholic solution of silicon fluoride to the action of a powerful battery, and afterwards subjecting the mercury to distillation, a small quantity of amorphous silicon was obtainable, but whether silicon, when in a nascent state, combines with or is soluble in mercury, still presents considerable doubt.

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ZIRCONIUM AND ITS ATOMIC WEIGHT.*

by G. H. BAILEY, D.Sc., Ph.D., The Owens College.

THE investigation described in the following paper was undertaken primarily with a view to the re-determination of the atomic weight of zirconium. In previous determinations the sulphate had been used by Berzelius (*Poggendorff Annalen*, vol. iv., p. 126) and Mats Weibull ("Om Zirkonium och dess föreningar"), the chloride and oxychloride by Hermann (*Journ. Prakt. Chem.*, vol. xxxi., p. 77), and the double fluoride of potassium and zirconium by Marignac (*Annales de Chimie*, vol. lx., 1860, p. 270). The results of these determinations are summed up in the following table, the relation O : H = 15·96 : 1 being used in the calculations.

	Mean determination.	Maximum.	Minimum.	Author.
$Zr(SO_4)_2 : ZrO_2$	89·23	89·42	89·05	Berzelius.
$Zr(SO_4)_2 : ZrO_2$	89·255	90·158	88·97	Mats Weibull.
$Zr : Cl_4$	88·56	—	—	Hermann.
$ZrO_2 : HCl$	89·915	90·76	89·07	,,
$K_2ZrF_6 : K_2SO_4$	90·31	92·57	89·84	Marignac.
$ZrO_2 : K_2SO_4$	90·47	90·97	90·02	,,
$K_2ZrF_6 : ZrO_2$	90·6	91·1	89·7	,,

The sulphate is somewhat readily decomposed by heat, the chloride and oxychloride are known to be unstable, and liable to considerable variation of composition according to the method of preparation, and the conditions under which these variations of composition are brought about were not understood, except in so far as the researches of Troost and others have indicated the great tendency which the salts show to pass into volatile and non-volatile oxychlorides of complicated character.

The determination is rendered difficult and unsatisfactory in consequence of—

(*a*). The difficulty of obtaining pure zirconia, and its separation from iron, titanium, and from silica.

(*b*). The tendency to form basic salts, and the hygroscopic character of its salts, and their general instability.

(*c*). The tenacity with which the hydrated zirconia retains the alkalies and smaller quantities of impurities in general.

Under these circumstances it seemed to me essential that any determination of the atomic weight of this element should be preceded by an inquiry into the best method of preparing pure zirconia, and an examinaton of the salts which might be made use of for the purpose, especially with reference to their stability.

Preparation of Crude Zirconia.

The raw material consisted of about 300 grms. of zircons from North Carolina, for which I was indebted to the kindness of Sir Henry Roscoe, and in addition to this a quantity of impure zirconia. The zircons were powdered by heating them to redness, and then throwing them quickly into cold water; they were then roughly powdered in an iron mortar, and finally in an agate mortar, and passed through linen. Part of this was treated with hydrogen potassium fluoride, the product being extracted with water, and re-crystallised many times from hot water. Prepared in this way, however, the zirconia was still impure, and showed the presence of iron in small quantities, and in addition to this it was extremely difficult to get rid of alkali.

The methods of fusion with sodium carbonate or acid potassium sulphate are troublesome and even less satisfactory.

Ultimately caustic soda and sodium fluoride were adopted for breaking up the zircons as recommended by Linnemann, and a modified form of the process followed out by him (*Monatsh. f. Chem.*, vol. vi., p. 337) was adopted as the most convenient. A mixture of 100 grms. of caustic soda and 10 grms. of sodium fluoride is heated in a covered silver dish over a large Bunsen burner, 25 grms. of finely powdered zircons are added in portions, the melt being kept stirred, and the heating continued for about an hour, or so long as there is any effervescence. The resulting mass is broken up and extracted with water, the residue consisting principally of sodium zirconate, but containing also silica and undecomposed zircon, oxide of iron, &c. This is now digested with dilute hydrochloric acid and filtered, the residue being subjected repeatedly to the same treatment. The acid solution containing the zirconium is evaporated to perfect dryness, and then exhausted with very dilute hydrochloric acid, and the silica filtered off. The process of solution and evaporation is repeated until the residue obtained dissolves completely in the acid. The impurity now present in the largest quantity is iron, and it was thought desirable to remove the bulk of this first. The hydrochloric acid solution is, therefore, evaporated to small bulk, and left to cool; the oxychloride of zirconium separates out in acicular crystals, leaving the iron in solution. The crystals are thrown into a funnel, and the liquid as far as possible removed at the pump, and the process of solution and separation of crystals in this way repeated several times. On precipitation of the final products with ammonia the crude zirconia is obtained, which forms the starting-point for further purification. In further operations, reagents (such as potassium or sodium salts) which could not be removed by volatilisation were avoided, and even at the present stage it was found necessary to re-dissolve the zirconia in hydrochloric acid, and re-precipitate with ammonia three times before the bulk of the sodium salts were got rid of.

Purification of the Crude Zirconia.

This crude zirconia, free from the impurities that occur in larger quantity, was dissolved in hydrochloric acid, and crystallised out as oxychloride. The aqueous solution of this, slightly acidulated, was treated with sulphuretted hydrogen for twenty-four hours; a gelatinous precipitate was obtained of a purplish black colour, consisting principally of sulphides of silver and copper, together with some hydrated zirconia. To the filtrate saturated with sulphuretted hydrogen was now added a little ammonia, which had the effect of bringing down a little more zirconia, and also small quantities of impurities precipitable by ammonium sulphide. The liquid was now acidulated and boiled down to get rid of the sulphuretted hydrogen, and excess of oxalic acid added to the concentrated solution to precipitate gadolinite earths, and finally treated with ammonium oxalate. There still remained some iron which had either not been removed or had been introduced in the course of treatment. To separate this, the oxychloride was crystallised repeatedly from concentrated hydrochloric acid, and finally washed with a mixture of the acid with one part of alcohol

* A paper read before the Royal Society, May 9, 1889.

and ten parts of ether. The only impurity that could now be detected was soda, which the zirconia retained with the greatest tenacity.

This was removed by precipitating the zirconia several times by means of ammonia, and re-dissolving it in hydrochloric acid. The zirconia finally precipitated by ammonia was washed* so long as any ammonium salts could be detected in the wash water.

The zirconia obtained was tested as to purity in the following way:—

(1). A portion treated with hydrofluoric acid showed no alteration in weight.

(2). The moist oxide dissolved completely in oxalic acid.

(3). On ignition it was perfectly white (inclined to a bluish cast), and a quantity exhausted with hydrochloric showed no trace of iron by the most delicate tests.

In order, however, to have a further guarantee that the product used for the determination of atomic weight had a definite composition and character, the experiments described later for the determination of atomic weight were made upon four portions, whose final treatment was as essentially different as possible.

Portion A was precipitated from an acid solution of the sulphate by the addition of hydrogen peroxide containing no other impurity than sulphuric acid.

Portion B was transformed into the tetrachloride by heating the zirconia with charcoal in a current of chlorine and then re-precipitating by ammonia.

Portion C was crystallised out from concentrated sulphuric acid by boiling off part of the excess of acid and then allowing to cool.

Portion D was further re-crystallised from hydrochloric acid, and washed very thoroughly with a mixture of hydrochloric acid, alcohol, and ether as described.

Stability of the Zirconium Salts.

In the case of zirconium it was evident that the number of compounds of a simple character and of sufficient stability to afford a good basis for a determination of atomic weight must be very limited. The principles, therefore, on which it was decided to proceed were—

(*a*). To prepare zirconia by several independent methods.

(*b*). To ascertain the most stable salt (or salts if more than one should prove stable), and the most simple transformation of this which would lead to an accurate determination.

Indeed, it seems to me in general that unless there are two or more salts of a very stable character, that reliance should lean rather towards the production of the raw material by independent processes, than towards the confirmation of results obtained from a more stable salt by means of values derived from observations on one that is less stable.

The methods previously used in the determination involved—

(1). Relation of zirconium sulphate to oxide.

(*a*). Direct conversion by ignition.

(*b*). *Vid* $BaSO_4$ by precipitation.

Mats Weibull (*loc. cit.*); Berzelius (*Pogg. Ann.*, vol. iv., p. 126).

(2). Relation of Zr (as ZrO_2) to Cl (as AgCl).

(*a*). By analysis of $ZrCl_4$.

(*b*). By analysis of $ZrOCl_2$.

Hermann (*Journ. Pr. Chem.*, vol., 97, p. 323).

(3). Relation of K_2ZrF_6 to ZrO_2 and to K_2SO_4. Marignac (*Ann. de. Chim.*, vol. lx., p. 257).

In addition to these it seemed possible that the relations—

(4). Zr to ZrO_2 by direct oxidation of the metal.

(5). Zr (as ZrO_2) to Br (as AgBr) on analysis of $ZrBr_4$, might be worthy of examination.

The bodies, therefore, to be investigated were the metal, the oxide, the chloride, the oxychloride, bromide, sulphate, and double fluoride. With regard to the last mentioned, no further investigation was considered necessary after the very complete treatment it has received at the hands of Marignac following upon the work of Berzelius on the double fluorides.

Preparation and Properties of Zirconium.

Zirconium was first obtained by Berzelius (*Poggendorff Annalen*, vol. iv., p. 117) by heating the anhydrous potassium zirconium fluoride with metallic potassium in an iron tube. It is described by him as being an amorphous black powder without lustre, and resembling charcoal in appearance. Becquerel, by electrolysis of a concentrated solution of the oxychloride, and Troost (*Journ. Prakt. Chem.*, vol. xcvii., p. 171), by fusing together potassium zirconium fluoride and aluminium, obtained it in a crystalline form, though it does not seem to have been in either case quite pure. Phipson (*Journ. Prakt. Chem.*, vol. xcvi., p. 447) found that, like carbon, boron, and silicon, it can be obtained by heating together magnesium and zirconia and then extracting the excess of magnesium and the magnesia by means of dilute hydrochloric acid.

There was left a black amorphous powder resembling that described by Berzelius. No determinations are, however, given to show how far this was free from impurity, and whether it contained unreduced oxide. A repetition of Phipson's experiments showed that, as far as the presence of foreign impurity is concerned, it leaves nothing to be desired, though I have not succeeded in preparing the metal by this or any other of the methods in a state of sufficient purity for a determination of atomic weight. Phipson's method is a very convenient one for preparing the metal, and the following results will show the conditions most favourable to its production in this way.

Experiments were first tried with intimate mixtures of magnesium powder, 3 grms. and 5 grms. respectively, with 4·4 grms. of zirconia, the mixture being heated to bright redness in an iron tube, the mouth of the tube being filled with finely powdered common salt. There remained, after repeated digestion with dilute hydrochloric acid, a fine black powder, so fine that it passed through the filter-paper and remained in part suspended for weeks in water, showing a reddish purple colouration by transmitted light.

When dried and heated in air to a point far below redness it glowed and was transformed into zirconia with a small increase in weight. It evidently consisted of zirconia containing only a small percentage of the metal. When rubbed in an agate mortar, however, it showed no white particles, and the variability of its composition, as shown in these and other experiments, lent no support to the assumption that a lower oxide had been formed. In a second set of experiments, magnesium foil was used, and in this case the foil retained its form, although permeated by metallic zirconium exactly as it does in the reduction of carbon compounds. By separating the foil from the finer powder it was possible to obtain zirconium almost free from oxide. Three specimens were prepared:—A resembled those already described, a velvety black powder, B had a slight greenish cast, and C a decided olive-green colour with a slight lustrous appearance.

It was thought, therefore, that A would prove to be the purest zirconium, judging from the experience of previous experimenters.

Samples were carefully heated in a stream of air, the moisture and carbonic acid (arising from carbon in the magnesium used) directly determined, and the proportion of Zr and ZrO_2 arrived at by calculation, knowing the

* Some of the earlier results had to be rejected because of incomplete washing. 20 grms. of zirconia required to be washed 150 times at the pump before ammonia salts were got rid of, at least 50 litres of water being used in the process.

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VOLUME LX.—1889.

LONDON:
PUBLISHED AT THE OFFICE, BOY COURT, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCLXXXIX.

LONDON:

PRINTED BY EDWIN JOHN DAVEY.

BOY COURT, LUDGATE HILL, E.C.

THE CHEMICAL NEWS.

VOLUME LX.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1545.—JULY 5, 1889.

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.*

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk-Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen, and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully dried powders of potash saltpetre and acetate of soda in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—nitrate of soda and acetate of potash.

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars; for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun nitrogen surrounded by its planets of hydrogen, and common salt (NaCl) may be looked upon as a double star formed of nitrogen and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrate visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor is capable of being destroyed. Therefore, in chemistry we must seek dynamic equilibrium, not only between the molecules, but also in their midst among their competent atoms. Many conditions of such equilibrium have been determined, but much remains to be done; and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of death-like inactivity.

* A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

heated for forty-five minutes on the water-bath. The flask is then cooled, the liquid made up to a known volume, and the acetic acid present is titrated by means of a standard solution of soda, using phenolphthalein as indicator. They then calculate to what quantity of monomethyl-aniline the acetic acid consumed must correspond, having of course deducted the quantity necessary for acetyling the aniline in the mixture.

Preparation and Purification of Amyl Iodide.—H. Malbot.—The author operates upon 240 c.c. of amylic alcohol, 20 grms. red phosphorus, and 200 grms. iodine. He eliminates the alcohol by means of very strong hydrochloric acid.

The Manganese Oxides obtained in the Moist Way.—Alex. Gorgen.—Hydrated manganous acid, in contact with an excess of precipitated manganous oxide, produces saturated manganite, $MnO_2 2MnO$. In presence of an excess of manganous carbonate it yields only an acid manganite, and in neutral solutions kept in that state manganous acid absorbs merely the quantity of manganous oxide corresponding to one of the acid manganites.

Action of Air on Manganese Carbonate. Can this Reaction give Rise to any of the Natural Peroxides?—A. Gorgen.—Not suitable for useful abstraction.

Zeitschrift fur Physikalische Chemie.
Vol. iii., Part 1.

The Origin of the Current in a Galvanic Combination.—L. Sohncke.—The author considers that the conception of fluidity founded by Clausius with the mere addition of a fundamental chemical fact seems capable of rendering readily intelligible the mechanism of the origin of a current in a galvanic circuit. The view of Clausius includes two hypotheses; that of contact and that of dissociation. The fundamental chemical fact is that different substances exert upon one and the same body chemical attractions of different strength.

The Conditions of Equilibrium between Chlorine and Iodine.—W. Stortenbeker.—This paper requires the accompanying illustrations.

The Action of Ferments.—G. Tammann.

On Raoult's Law of Congelation.—R. Fabinya.—Both these papers require the accompanying figures and tables.

MISCELLANEOUS.

Improved Balance.—At the Hamburg Exhibition of Trades and Industries Max Beckel displays an analytical balance, the sensitiveness of which can be modified at pleasure.—*Chemiker Zeitung.*

Sewage Treatment at Kingston-on-Thames.—On Saturday, June 29th, the works for the treatment of the sewage of Kingston and Surbition were formally inaugurated in presence of a numerous gathering of municipal authorities, medical practitioners, chemists, engineers, and others interested in sanitary questions. The process adopted is that form of the absorption-precipitation system known as the "A B C," and is conducted by the Native Guano Company, Limited. The offensive matters are first absorbed or occluded by the addition of finely ground clay and carbon, and the whole is then treated with a salt of aluminium. The mixture is then allowed to subside in a series of tanks; whence the effluent water passes out to the Thames, clear, inodorous, and having that faintly blue tint which marks the removal of dissolved organic impurities. So complete was the deodorisation that, though the day was hot and almost calm, the visitors, when sitting down to lunch in a marquée on the leeward side of the works, tanks, &c., could perceive no offensive smell. The works, as at present constructed, meet the requirements of 38,000 people, and we are told that with some comparatively trifling additions they can be arranged for a population of 50,000.

Determination of Phosphoric Acid in Superphosphate.—Julius Stoklasa.—10 grms. of the sample are placed in one litre of water. Of the filtrate 50 c.c. are mixed with a solution of ammonium citrate and magnesia mixture, and well shaken for five to six minutes in a shaking apparatus. Ammonia is then added to the extent of one-fourth of the entire volume of liquid. The magnesium ammonium phosphate is then filtered in a perforated platinum crucible; in this it is washed, ignited, and weighed as pyrophosphate. The ammonium citrate solution is obtained by dissolving 250 grms. citric acid in ½ litre of water and using 20 c.c. of this solution, after being neutralised with ammonia.—*Chemiker Zeitung (Costhen).*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Thiocamf.—I should be much obliged if any of your correspondents could let me know where I could purchase the new disinfectant, thiocamf, described on p. 291, vol. lix., Chemical News, June 21, 1889.—G. E. Wright.

Prof. A. E. FOOTE,

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THE CHEMICAL NEWS.

Vol. LX. No. 1546.

THE CONDITIONS OF ACTION OF NITRIC ACID.

By C. F. CROSS and E. J. BEVAN.

The appearance of a paper by Mr. V. H. Veley on this subject, or rather upon one aspect of it, affords a convenient opportunity of recording some experimental results which have accumulated during the last year or two, bearing upon this question of the exact mechanism of the actions of nitric acid. The directions of investigation have been various, and we briefly record the main results under their respective heads.

Action of Dilute Nitric Acid upon Ligno-celluloses with and without Addition of Urea.—Our observation that the presence of urea arrests the specific action of nitric acid upon the lignified celluloses, changing it into one of simple hydrolysis, as in the case of the stable mineral acids, is recorded in "Watts's Dic.," New Ed., Art. "Cellulose." We take from our note-book (1887) the following record of experiments:—

(*a*). Four portions of jute fibre of 2 grms. each; with 50 c.c. of nitric acid of 1·05 sp. gr.; weights of urea added, 0·1, 0·2, 0·3, 0·4 respectively; digested seven hours at 60° to 70°. The fibrous residues were then washed, dried, and weighed. The results are given as percentage yield, with the external characteristics of the products:—

(1).	68·0	per cent.	Pale yellow, approximating to cellulose.
(2).	71·1	,,	Brownish yellow.
(3).	75·4	,,	Reddish yellow.
(4).	77·2	,,	Mahogany red, differing but little from the original.

With the graduated increase of urea there is a gradual departure from the characteristic action of the pure acid, which we have investigated and described on previous occasions, and in regard also to the soluble products of the reaction in which corresponding variations between the two extremes were observed. To complete the above series we may mention that under these conditions of digestion of the fibre with the pure dilute acid the reduction to cellulose is complete, the yield amounting to 60—65 per cent. It is scarcely necessary to say that by largely increasing the urea—added in the form of nitrate—beyond the maximum proportion above given an even greater divergence may be determined, and as the results are very evident to the senses, the comparison makes a striking lecture demonstration.

These results led us to extend the investigation of the influence of urea—*i.e*, of the elimination of nitrous acid—to other actions of nitric acid. We exposed metallic copper—as Mr. Veley has done—in the form of a wire spiral ($\frac{1}{8}$ in.) of the pure metal, to acid of 1·05 sp. gr. at 60°, with and without the addition of urea, the quantity of acid being 50 c.c., and of copper 4·465 in two comparative experiments. In the case of the pure dilute acid a digestion of four hours was required for the complete dissolution of the metal. With the addition of 1 grm. urea, the weight lost at the expiration of three hours was only 0·020 grm. Further, similar experiments afforded us sufficient evidence of what Mr. Veley has now proved by means of his carefully elaborated method, viz.. that the interaction of nitric acid and the metals is another instance of dependence upon the *tertium quid*, which in this case could scarcely be other than nitrous acid.

Action of "Nitrating" Mixture ($HNO_3+H_2SO_4$) *with and without Addition of Urea.*—It appeared that the investigation of this point might throw further light upon the formation and constitution of the explosive derivatives obtained from the celluloses and compound celluloses. We made a series of comparative "nitrations," both of cotton and the jute fibre, with and without addition of urea to the acid mixture. The evidence as to its influence on the reaction was uniformly negative, a result which strengthens the evidence that the derivatives in question are alcoholic nitrates. When, on the other hand, the formation of a nitro-derivative is involved, the presence of urea may have a very important influence, as indeed Dr. Perkin, Jun., showed in a recent note communicated to the Chemical Society on the "Nitration of Anthracene in Presence of Urea," this modification of the conditions being proved to determine a simple substitution in the carbon nucleus.

The last point to which we desire to call attention is a decomposition which would appear to stand in direct contrast to those already discussed, although, like these in illustrating the dependence of reactions upon an intermediary third substance; the reaction in question is the *complete combustion of urea by chromic acid, in presence of nitric acid.* In the course of working out the method of ultimate analysis of carbon compounds by combustion with chromic anhydride in presence of sulphuric acid (*Chem. Soc. J.*, 1888, 889), we observed that the decomposition of nitrogen compounds was generally very incomplete. Recalling the fact that urea survives the very severe combustions of the animal body, we made experiments upon this compound and found in effect that it entirely resisted the action of the chromic mixture. On one occasion we happened to employ a silver chromate prepared by precipitation from the nitrate, and were surprised to find that a rapid combustion ensued, resulting in the complete conversion of the urea into gaseous products (CO_2+N_2). Investigation of this particular specimen of chromate showed it to contain a small quantity of residual nitric acid. That this was the determining agent in the decomposition was shown by direct experiments, of which the following are the details:—

(1). Urea taken, 0·1509; 9 c.c. H_2SO_4 with excess of CrO_3 (1—2 grms.) and 0·500 grm. KNO_3.
Vol. of gas collected, 121 c.c. at 20° and 756 m.m.
Corrected vol., 112·7 c.c.
Deducting vol. of nitrogen, calc.—

$$\frac{0{\cdot}0703}{1{\cdot}256} \times 1000 = 56 \text{ c.c.}$$

leaves 56·7 c.c. CO_2, from which carbon percentage of urea = 20·1 (calc., 20·0).

(2). 0·1502 urea. Conditions as in (1).
Vol. of gas collected, 121·5 c.c. at 19° and 755 m.m.
Corrected vol., 113·0. Taking one-half as CO_2 and calculating the carbon percentage we obtain 20·2.

(3). 0·1522 urea. Conditions as in (1).
Vol. of gas collected, 125·0 c.c. at 20° and 752 m.m.

$$\text{Carbon percentage calc. from corr. vol.} = \frac{115{\cdot}2}{2} = 20{\cdot}2.$$

These numbers are higher than those obtained in the combustion of nitrogen-free compounds by this method, the slight absorption of the gaseous products by the sulphuric acid appearing to be exactly balanced by the tension of the nitric acid added. Similarly, in regard to this latter point, we found that picric acid, which yielded at once to the acid mixture, the combustion completing itself rapidly, yielded a volume of CO_2, from which the percentage number calculated was identical with the theoretical. In this case it was of course unnecessary to add nitric acid. Aniline, which we had been unable to burn satisfactorily with the chromic mixture, underwent complete combustion in presence of nitric acid, added as in the above experiments. The numbers obtained (percentage) were constant, and again slightly in excess of

the theoretical. In this case no nitrogen was evolved, being entirely retained by the acid as ammonia.

Reverting now to the question of the equilibrium of the urea molecule, we find that under the conditions of this combustion it is stable, but that the introduction of nitric acid suffices to upset it. Its influence in determing the rupture of the molecule would appear to be specific, for we found that vanadium pentoxide, which from all analogies might be expected to behave similarly, was entirely without influence. To explain the specific action of the nitric acid, according to the generally received view, we must assume reduction to the lower state of oxidation and contact in this form with the amide nitrogen, with the usual result: $2NH_3+N_2O_3=3H_2O+2N_2$. It is difficult, however, to see how this can take place, even locally, under such powerful oxidising conditions. Anticipatory explanations have, moreover, little value outside a text-book; if adopted in the laboratory they rather obstruct by making appear unnecessary the prosecution of the search for the actual cause up to the limits of the experimental method. We confess our inability to offer an adequate explanation: but the fact is for the present more important. We shall continue our investigation of these points as opportunity offers, but without wishing to make any reservation to ourselves in so wide a field of research on account of priority. Mr. Veley having announced his intention of extending his researches to other metals, using the methods described, we willingly relinquish this portion of the subject with a due acknowledgment of the perfection of detail of his methods. But in regard to the general study of the conditions of action of nitric acid, we should expect that most chemists engaged in research could contribute some observations which, if gathered together from all sources, would make an imposing and interesting chapter in chemical mechanics.

4, New Court, Lincoln's Inn,
June 28, 1889.

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

We have learnt with deep regret of the demise of our highly valued contributor, Mr. David Lindo, of Falmouth, Jamaica. He died on May 7th after a painful illness of six weeks, during which he had to undergo the operation of lithotomy. His executor has kindly forwarded to us the notes of an incomplete investigation on the analysis of glass which our late correspondent had taken up a few months prior to his end. His attention had been drawn to this subject as he had found most of his beakers, test-tubes, &c., became cloudy within. On testing them with phenolphthalein he found that not merely the cloudy glasses, but those also which were to all appearance perfectly clear and bright, turned a rich magenta colour when the test was applied.

For the determination of silica in the several samples 2 grms. of the glass in very fine powder were taken. The author took first something over 2 grms. in small fragments, which, after weighing, were crushed in the steel mortar, ground fine in a large agate mortar, transferred to a platinum crucible, ignited gently, placed in the desiccator, carried to the balance while warm, and two grms. exact were quickly weighed out. The glass was then fused in a large platinum crucible with 8 grms. of alkaline mixture (13 parts potassium carbonate and 10 parts sodium carbonate), heating first gently, then more strongly for half an hour more with large concentric spirit-lamp, and then for a quarter of an hour with blast-lamp urged with multiple blowpipe; the crucible was cooled generally in water after spreading the fusion over the surface, some distilled water added to contents, and heated some time on sand-bath, which treatment nearly dissolved out the contents, which were then transferred to a beaker. More water was then added to the residue in the crucible and heated cautiously by means of a spirit-lamp, moving the latter about under the crucible and not allowing the contents to boil. In this way the residue was easily dissolved out, transferred to the beaker, and rinsed well; finally, with the HCl to be used for decomposition, he rinsed the cover of the crucible in the acid, and covered the beaker with a clock-glass. He then added the acid cautiously (30 c.c. HCl, diluted with the washings of the crucible). After heating for some time on the sand-bath the whole was transferred generally the next day to a large platinum dish, evaporated to dryness, reduced to powder with an agate pestle, and heated about two hours longer on the sand-bath. It was then moistened with 6 or 8 c.c. HCl and a little water, let rest for several hours, though it is not absolutely necessary to wait so long. There were then added 60 c.c. of water, the whole was heated and filtered into a 200 c.c. flask, washed well with hot water, the washings concentrated and added to the contents of the flask. The silica was dried in the stove, placed in a platinum crucible, the filter was burnt, and its ash put into the crucible and mixed with 6 or 7 grms. alkaline mixture. The whole was then fused again as above, and dissolved out again as before; the solution was always brilliantly clear. To get the silica in a vitreous form it was sufficiently diluted with water before adding the 25 c.c. HCl. In one or two instances the silica was partly precipitated, the dilution not being sufficient. He proceeded as with the first or crude silica, except that the quantity of water was 50 c.c. instead of 60 c.c., and the silica was collected in a Gooch crucible, and the filtrate and concentrated washings were added to the contents of the flask. 200 c.c. of hot water are quite sufficient to wash this silica provided it is all in the vitreous form, as it is then washed much more easily than when it is in the ordinary amorphous condition. Hence it is always better to obtain silica in the vitreous state. The greater dilution which this requires renders the evaporation more tedious, but this is more than compensated by the more rapid and satisfactory washing. The silica is always beautifully white. A little, of course, passes into solution, as the ammonia precipitates are often insufficient to carry this dissolved silica down. The author therefore prepared some ferric chloride containing a slight excess of HCl, and precipitated 10 c.c. in the flask with ammonia in slight excess. He then filtered through a Gooch, washed well with hot water, ignited, and weighed. By this means the last trace of silica was recovered from the solutions. The silica will therefore generally be separated—(1). From the whole mass of salts (which may be called the bulk). (2). From the ammonia precipitates. (3). From the filtrate given by ammonia, carrying down the last trace with ferric oxide. The bulk was ignited first with the spirit-lamp, and then heated for eight minutes with the flask. On this there was no further loss. The small residues were ignited with the larger spirit-lamp, using the mouth blow-pipe.

No. 28. In a 300 c.c. cloudy flask the percentage of silica found was 73·13.

No. 10. Some test-tubes *not* cloudy yielded 68·94 per cent silica.

No. 3. In other test-tubes which were turning cloudy, and which when pulverised appeared deeply blue from the presence of manganese, the silica was 70·61 per cent.

No. 22. A cloudy pint tumbler (moulded) yielded a bluish green mass, not very dark, and contained 73·06 per cent of silica.

No. 29. A 300 septem flask, *not* cloudy, giving a mass coloured deeply blue with manganese, contained 71·49 per cent silica.

No. 34A. French glass tubing, *not* cloudy, giving a deep blue mass, yielded 69·86 per cent of silica.

No. 34B. French glass tubing, not cloudy (part of same tube as the foregoing), contained 70·11 per cent of silica.

No. 8. Pipette, cloudy mass, blue with manganese, gave 67·23 per cent of silica.

No. 1. Clear flask, reacting strongly with phenolphthalein and forming a blue mass (manganese), showed 72·42 per cent of silica.

No. 5A. 100 c.c. flask, turned cloudy, mass white, containing no manganese. The silica was 72·96 per cent.

No. 31. Clear retort glass, reacting slightly with phenolphthalein, and yielding a deep blue mass with a violet reflection. Silica, 73·70 per cent.

(To be continued).

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.*

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

(Continued from p. 4).

BUT while speaking of the application of the principle of substitution to water, we need not multiply instances, but must turn our attention to two special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyd, C_2H_4O, which, as its very name implies, is "alcohol dehydrogenatum," or alcohol deprived of hydrogen. Hence aldehyd combined with hydrogen yields alcohol; and united to oxygen acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the de-oxidisation of nitric acid and the oxidisation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water; $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid, as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid, are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH, are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2; and such are hydrogen and the peroxide thereof. In general, if a molecule AB exists, then molecule AA and BB can exist also. A direct reaction of this kind does not, however, take place in water; therefore undoubtedly, at the moment of formation hydrogen reacts on the peroxide of hydrogen, as we can show, at once, by experiment; and, further, because the peroxide of hydrogen, H_2O_2, exhibits a structure containing a molecule of hydrogen, H_2, and one of oxygen, O_2, either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, peroxide of hydrogen is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases; and in the peroxide of hydrogen we actually have such equal volumes of the elementary gases.

The instability of peroxide of hydrogen—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous bodies—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decomposition of water. I may mention this additional consideration that, with respect to the peroxide of hydrogen, we may look for its effecting still further substitutions of hydrogen by means of which we may expect to obtain still more highly oxidised water-compounds, such as H_2O_3 and H_2O_4. These Schönbein and Bunsen have long been seeking, and Berthelot is investigating them at this moment. It is probable, however, that the reaction will stop at the last compound, because we find that, in a number of cases, the addition of 4 atoms of oxygen seems to form a limit. Thus, OsO_4, $KClO_4$, $KMnO_4$, K_2SO_4, Na_3PO_4, and such like, represent the highest grades of oxidation.*

As for the last forty years, from the time of Berzelius, Dumas, Liebig, Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butlerow, most theoretical generalisations have centered round organic or carbon compounds, so we will, for the sake of brevity, leave out the discussion of ammonia-derivatives, notwithstanding their simplicity in respect to the doctrine of substitutions; we will dwell more especially on its application to carbon compounds, starting from methane, CH_4, as the simplest of the hydrocarbons, containing in its molecule one atom of carbon. According to the principles enumerated we may derive from CH_4 every combination of the form CH_3X, CH_2X_2, CHX_3, and CX_4, in which X is an element, or radical, equivalent to hydrogen, that is to say, competent to take its place or to combine with it. Such are the chlorine substitutes mentioned already, such is wood-spirit, $CH_3(OH)$, in which X is represented by the residue of water, and such are numerous other carbon derivatives. If we continue, with the aid of hydroxyl, further substitutions of the hydrogen of methane, we shall obtain successively $CH_2(OH)_2$, $CH(OH)_3$, and $C(OH)_4$. But if, in proceeding thus, we bear in mind that $CH_2(OH)_2$ contains two hydroxyls in the same form as peroxide of hydrogen, H_2O_2 or $(OH)_2$, contains them—and moreover, not only in one molecule, but together, attached to one and the same atom of carbon—so here we must look for the same decomposition as that which we find in peroxide of hydrogen, and accompanied also by the formation of water as an independently existing molecule; therefore $CH_2(OH)_2$ should yield, as it actually does, immediately water and the oxide of methylene, CH_2O, which is methane with oxygen substituted for two atoms of hydrogen. Exactly in the same manner out of $CH(OH)_3$

* A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

* Because more than four atoms of hydrogen never unite with one atom of the elements, and because the hydrogen compounds (*e.g.*, HCl, H_2S, H_3P, H_4Si) always form their highest oxides with four atoms of oxygen, and as the highest forms of oxides (OSO_4, RO_4) also contain four of oxygen, and eight groups of the periodic system, corresponding to the highest basic oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, R_2O_7, and RO_4, imply the above relationship, and because of the nearest analogues among the elements—such as Mg, Zn, Cd, and Hg; or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br, and J, and so forth—not more than four are known, it seems to me that in these relationships there lies a deep interest and meaning with regard to chemical mechanics. But because, to my imagination, the idea of unity of design in Nature, either acting in complex celestial systems or among chemical molecules, is very attractive, especially because the atomic teaching at once acquires its true meaning, I will recall the following facts relating to the solar system. There are eight major planets, of which the four inner ones are not only separated from the four outer by asteroids, but differ from them in many respects, as, for example, in the smallness of their diameters and their greater density. Saturn with his ring has eight satellites, Jupiter and Uranus have each four. It is evident that in the solar systems also we meet with these higher numbers four and eight which appear in the combination of chemical molecules.

are formed water and formic acid, CHO(OH), and out of $C(OH)_4$ is produced water and carbonic acid, or directly carbonic anhydride, CO_2, which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated —they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain bodies of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3, that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself, then by substituting this group for the original hydrogen, we obtain acetic acid, $CCH_3O(OH)$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formiate, $CHO(OCH_3)$. These bodies differ so much from each other physically and chemically that, at first sight, it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, while its metamer, formo-methylic ether, is lighter than water, and boils at 30°, that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways:—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.
2. Into a group CH_2 and H_2. We will call this order of substitution methylenation.
3. Into CH and H_3, which commutations we will call acetylenation.
4. Into C and H_4, which may be called carbonisation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4, which contains four atoms of hydrogen by the first three methods of substitution; carbonising would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say, strongly polyatomic, as I have long since been proving by various means—could contain only C_2, like the molecules O_2, H_2, N_2, and so on.

By methylation we should evidently obtain from marsh gas, ethane, $CH_3CH_3=C_2H_6$.

By methylenation, that is by substituting group CH_2 for H_2, methane forms ethylene, $CH_2CH_2=C_2H_4$.

By acetylenation, that is by substituting three atoms of hydrogen, H_3, in methane, by the remnant CH, we get acetylene, $CHCH=C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can not only produce those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3, and the substitution of the hydrogen by hydroxyl. The following are the possible changes:—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O.

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Wurtz, which has shed so much light on the history of alcohol. Its isomer may be $CH_3CH(OH)_2$, but as we have seen in the case of $CH(OH)_2$, it decomposes, giving off water, and forming aldehyd, CH_3CHO, a body capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyd, CH_3CHO, but its isomer,—

$$\begin{matrix} CH_2CH_2 \\ O \end{matrix},$$

the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid $OH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, CHO(OH), with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction, and the greatest viscosity, when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently alcoholic acid, and, indeed, this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomers, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, aldehyd of oxalic acid, or the glyoxal of Debus, CHOCHO.

5. $CH(OH)_2C(OH_3)$, from the tendency of all the preceding, corresponds to glyoxylic acid, aldehyd acid, CHOCO(OH), because the group CO(OH), or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyd function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid, CO(OH)CO(OH), which generally crystallises with $2H_2O$, following thus the normal type of hydration characteristic of ethane.*

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyd alcohols, aldehyds, alcohol acids, and the acids, but also

* One more isomer, $CH_2CH(OH)$, is possible, that is secondary vinyl alcohol, which is related to ethylene, CH_2CH_2, but derived by the principle of substitution from CH_4. Other isomers of the composition C_2H_4O, such, for example, as $CHCH_2(OH)$, are impossible, because it would correspond to the hydrocarbon $CHCH_3=C_2H_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomer existed, it would be derived from CH_3, but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity, and then rejects it, the facts serving to establish either one or the other view; and therefore, it seems to me, that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as, in their time, was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to abandon the structural theory. They will all be united in chemical mechanics, and the principle of substitution must be looked upon only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and Van't Hoff, may yield points of departure.

combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated, substances of which ethylene, CH_2CH_2, and acetylene, CHCH, are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves:—CH_3CHX_2 and CH_2XCH_2X, although both contain $C_2H_4X_2$, or CH_2CX_2 and CHXCHX, although both contain $C_2H_2X_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyd and the oxide of ethylene, to which we have already referred, because both have the composition C_2H_4O.

(To be continued).

ZIRCONIUM AND ITS ATOMIC WEIGHT.*

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

(Continued from p. 8).

Zirconium Peroxide, ZrO_3.

CLEVE (*Paris Soc. Chim. Bull.*, vol., xliii., p. 53) precipitated an oxide, to which he assigned the composition ZrO_3, by adding ammonia and hydrogen peroxide to a solution containing a zirconium salt; my own experiments (*Chem. Soc. Journ.*, vol xlix., p. 481), in which the oxide was precipitated from a dilute solution by the addition of hydrogen peroxide alone, the solution being slightly acid, gave an oxide agreeing well with the composition Zr_2O_5; it was found also that an oxide resembling Clève's could be obtained without the addition of ammonia. In order to see whether the peroxide, ZrO_3, was identical with that obtained by Clève, I precipitated a large quantity of a moderately concentrated solution of zirconium sulphate, containing a slight excess of acid—

(*a*). By the addition of hydrogen peroxide alone.
(*b*). By the addition of hydrogen peroxide, and then ammonia, until just alkaline.

	Mean determinations. (*a*).	(*b*).	Calculated for ZrO_3.
Zr	64·92	64·97	65·21
O	35·08	35·03	34·79

It is evident, therefore, that with due precaution an oxide agreeing very definitely with the formula ZrO_3 is obtainable by precipitation with hydrogen peroxide, either in alkaline or acid solution. The addition of ammonia, especially in excess, is, however, not to be recommended, since it tends to bring down the ordinary oxide, and to decompose the hydrogen peroxide added, with the production of nitrous and nitric acid. Dried for several weeks over phosphorus pentoxide, the oxide became constant in weight, and showed the composition $ZrO_3.3H_2O$, the hydrate of zirconia being $ZrO_2.2H_2O$. The salt, however, lost about 2 per cent of oxygen during the process of drying, and if this were carried out at 100° it had the composition Zr_2O_5.

Zirconium Tetrachloride.

About 30 grms. of this salt were prepared in the usual way, by passing dry chlorine over a mixture of charcoal and zirconia. If a determination was to be made from this salt some process of purification was necessary, and a criterion that a body of constant composition had been obtained, especially as it is known that volatile oxychlorides exist.

For this purpose a combustion-tube, in which the chloride was prepared, was drawn out into a series of bulbs, separated by constrictions. The chloride was then sublimed (a lower temperature being used for each successive bulb) in a current of dry chlorine into these bulbs, which were separately sealed off and their contents analysed. It was hoped in this way that two or more bulbs would be obtained showing concordant results, but, notwithstanding that every precaution was taken to exclude air and moisture, no such result could be achieved, and decomposition was clearly indicated to have taken place with the formation of traces of a reddish brown product, the equivalent of chlorine in relation to zirconium being in some cases higher and in others lower than four to one. Furthermore, in no case was it found possible to prepare such a product perfectly free from silica or iron. It seems, indeed, that zirconium tetrachloride is even more liable to dissociation and decomposition than the corresponding silicon compound.

Zirconium Oxychloride.

This salt is prepared, as already stated, by crystallisation from concentrated hydrochloric acid. The difficulties attending its preparation in the pure state arise from the presence of free hydrochloric acid and from the readiness with which the salt passes into oxychlorides of a more basic character. Berzelius attempted to remove the excess of free acid by heating the salt to 60°, but was not able to obtain a definite product, his numbers being—

ZrO_2	0·332	0·485
AgCl	0·661	1·096

whereas the silver chloride should be about 2½ times the amount of the ZrO_2. Paykull (*Paris Soc. Chim. Bull.*, vol. xx., p. 65) dried the salt between filter-paper, and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by excess of HCl being $2ZrOCl_2.13H_2O$.

Basic oxychlorides, $Zr_3O_4Cl_4$ (Endemann), $Zr_2O_3Cl_2$, Zr_2OCl_6 (Troost and Hautefeuille), ZrOClOH, $Zr_8O_8Cl_7(OH)_9$ (Endemann), have also been described.

The salt examined by me was prepared by repeated crystallisation from concentrated hydrochloric acid, washed with hydrochloric acid till the washings were colourless and showed no trace of iron, and then the free acid removed—

(*a*). By washing with a mixture of 1 part of alcohol and 10 parts of ether.
(*b*). By gently heating the salt.
(*c*). By exposing the finely powdered salt at ordinary temperature in a vacuous desiccator over potash, until no HCl appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid, and precipitating the chlorine by means of silver nitrate.

In the following tables are given Berzelius's determinations and those obtained by using the methods (*a*) and (*c*).

(*b*) is omitted, since it was found that a constant and progressive diminution of chlorine occurred during the process. It will be sufficient for the purpose to state simply the relation of ZrO_2 to AgCl obtained.

	ZrO_2.	AgCl.
(1). Berzelius's determination	1 :	1·991
,, ,, ...	1 :	2·260
(*a*). Washed with ether and alcohol ..	1 :	2·206
	1 :	2·179
	1 :	2·226
	1 :	2·260
(*c*). Exposed *in vacuo* over KHO ..	1 :	2·264
Without washing	1 :	2·245
	1 :	2·309
	1 :	2·285
$ZrOCl_2$(Zr = 90)	1 :	2·350

* A Paper read before the Royal Society, May 9, 1889.

The whole of the specimens analysed dissolved in water to a clear solution, with a slightly acid reaction. The determination which shows the highest proportion of chlorine would give the atomic weight of zirconium as 92, which is, undoubtedly, too high, and, moreover, it will be quite evident from these numbers that no trustworthy determination was to be expected from this salt.

The Tetrabromide.

This salt was prepared by heating zirconium in an atmosphere of bromine vapour, but proved no more promising in its behaviour than the corresponding chlorine derivative.

The Sulphate.

Several methods of preparing the sulphate were tried, but ultimately that originally used by Berzelius was adopted. Finely powdered zirconia (air-dried) was heated with concentrated sulphuric acid, and most of the excess of acid driven off at as low a temperature as possible. In order to obtain the normal sulphate Berzelius drove off the excess of sulphuric acid, and then heated for a quarter of an hour, but never to redness; Mats Weibull heated till constant at 300°; a temperature manifestly too low. Clève, in a private communication, advised me to heat in a sulphur-bath (442°). It seemed, however, that in this instance, where the atomic weight depended on determinations from the sulphate alone, and especially since this is a general method applicable to several other elements, it was desirable that the limits of temperature within which the normal sulphate was stable should be ascertained. This was done in the case of a number of sulphates (Bi, Mg, Tn, Di), and the details of the investigation have already appeared (*Chem. Soc. Journ.*, vol. li., p. 676).

The salt containing excess of sulphuric acid was heated in a bath, described in that communication, which could be easily kept within 5°, at any temperature up to 500°. The boat containing the salt was weighed from time to time until it became nearly constant. The salt was then finely powdered, and the heating continued in periods of about four hours, until no further diminution of weight occurred, showing that the free sulphuric acid had been got rid of. The temperature of the bath was now raised by intervals of about 10°, and the heating continued for several hours at each limit, weighings being made after each increment until a point was arrived at at which loss of weight was again observed. This indicated that the temperature had been attained at which the normal salt began to undergo decomposition. We have then the limits of temperature within which the normal sulphate is stable. Several series of determinations were made, and one of these is given to show the character of the values obtained.

	Grms.
Weighing tube and boat	20·64962
,, ,, and salt	22·9095
After heating 6 hours at 300°	22·9045
,, 7 ,, 330	22·9015
,, 4 ,, 350	22·9002
,, 4 ,, 365	22·90012
,, 5 ,, 380	22·90025
,, 4 ,, 390	22·90020
,, 4 ,, 410	22·89820

The above numbers have not had applied to them the small corrections for variations of barometer and thermometer, and no importance need be attached to the differences of one- or two-tenths of a m.grm. between 350° and 400°.

It appears, therefore, from these experiments that zirconium sulphate is stable up to 400°, and that the excess of sulphuric acid is driven off completely at 350°. If, therefore, a mixture of the salt and the free acid, prepared as above, be heated at any temperature between 350° and 400° till constant, we shall obtain the normal sulphate. The temperature of the sulphur-bath would be too high, and of course at dull redness decomposition would set in.

(To be continued).

ON THE

OCCURRENCE OF PARAFFIN IN CRUDE PETROLEUM.*

By E. A. PARTRIDGE, University of Pennsylvania.

It is well known that paraffin obtained by the distillation of petroleum residues is crystalline, while that obtained directly (as in the filtration of residuum) is amorphous. Ozokerite or ceresine differs but slightly from paraffin, the principal distinction being want of crystalline structure in it as found. Other characteristics, such as the melting-point, specific gravity, &c., vary in both, and so are not of importance in a comparison. Hence it has been asked, is the paraffin occurring in petroleum and ozokerite identical with that which is produced by their distillation? As crystalline paraffin could be obtained from ozokerite by distillation alone, many persons have supposed that it was engendered in the process. Recently, however, crystalline paraffin has been obtained from ozokerite by dissolving the latter in warm amyl alcohol; on cooling, the greater part separates out in crystals having the lustre of mother-of-pearl. By repetition of this process, a substance is obtained that is scarcely to be distinguished from the paraffin obtained by distillation. Apparently there exists then in ozokerite, together with paraffin, other substances not capable of crystallisation which keep the paraffin from crystallising. These colloids appear to be separated by amyl alcohol in virtue of their great solubility in that menstruum. It is also reasonable to suppose that they undergo change or decomposition by distillation.

So as petroleum residues are amorphous, and the crystalline paraffin is first produced by distillation, it has been argued that the paraffin present in crude petroleum is approximately the same thing as ozokerite.

This, however, is not sufficient to establish the pyrogenic origin of all crystallised paraffin, as crystals can be obtained from the amorphous residues by distillation at normal or reduced pressure, or in a current of steam. To explain these facts two assumptions are possible. Either the chemical and physical properties of all or some of the solid constituents are changed by the distillation, and the paraffin is changed from the amorphous into the crystalline variety, or the change produced by the distillation takes place in the medium (*i.e.*, the mother liquid) in which the paraffin exists. The change effected in ozokerite and in petroleum residues when crystalline paraffin is obtained by distillation, is to be regarded as a purification, and can be effected partly by treatment with amyl alcohol. In the same way, by repeated treatment of petroleum residuum with amyl alcohol, a substance of melting-point 59° C. can be obtained, which cannot be distinguished from ordinary paraffin.

The treatment with amyl alcohol has therefore accomplished the same results as were obtained by distillation, and the action is probably the same, *i.e.*, a partial separation of colloid substance. These facts point to the conclusion that crystallisable paraffin exists ready formed in both petroleum and in ozokerite, but in both cases other colloidal substances prevent its crystallisation. By distillation, these colloids appear to be destroyed or changed so as to allow the paraffin to crystallise.

It is a generally known fact that liquids always appear among the products of the distillation of paraffin, no

* An Abstract of a Thesis read before the Chemical Section of the Franklin Institute.

matter in what way the distillation be conducted. This shows that some paraffin is decomposed in the operation.

The name *proto-paraffin* has been given to ozokerite, and to the paraffin of petroleum in contra-distinction to *pyro-paraffin*, the name that has been applied to the paraffin obtained by distillation from any source.

According to Reichenbach, paraffin may crystallise in three forms: needles, angular grains, and leaflets having the lustre of mother-of-pearl. Hofstädter, in an article on the identity of paraffin from different sources, confirmed this statement, and added, further, that at first needles, then the angular forms, and then the leaflets are formed. Fritsche found, by means of the microscope, in the ethereal solution of ozokerite, very fine and thin crystal-leaflets concentrically grouped, and in the alcoholic solution fine irregular leaflets. Zaloziecki has recently developed these microscopic investigations to a much greater extent. According to this observer, the principal part of paraffin, as seen under the microscope, consists of shining stratified leaflets with a darker edge. The most characteristic and well-developed crystals are formed by dissolving paraffin in a mixture of ethyl and amyl alcohols, and chilling. The crystals are rhombic or hexagonal tablets or leaves, and are quite regularly formed. They are unequally developed in different varieties of paraffin. The best developed are those obtained from ceresine. Their relative size and appearance give an indication as to the purity of the paraffin, and, as they are always present, they are to be counted among the characteristic tests for paraffin. Reichenbach observed that mere traces of empyreumatic oil prevented their formation.

The old method of determining the amount of paraffin in petroleum was to carry out the refining process on a small scale; that is, to distil the residue from the kerosene oils to coking, chill out the paraffin, press it thoroughly between filter-paper, and weigh the residue. The sources of error in this procedure are manifold; the principal one is the solubility of paraffin in oils, which depends upon the character of both the paraffin and the oil, and also upon the temperature. The next greatest source of error is variation in the process of distillation, and the difference between working on the small scale and on the large scale.

In most cases, where a paraffin determination is to be carried out, one has to deal with a mixture of paraffin with liquid oils. Now, paraffin is not a substance defined by characteristic physical properties which distinguish it from the liquid portions of petroleum. It consists of a mixture of homologous hydrocarbons, which form a solid under ordinary conditions. The hydrocarbons of this mixture show a gradation in their properties, and gradually approximate to those which are liquid at ordinary temperatures. It is a well-known fact that a separation of these homologues is entirely impossible by distillation. It has also been ascertained that the liquid constituents of petroleum do not always possess boiling-points that are lower than those of the solid constituents. This shows that we have to deal not merely with hydrocarbons of one but of several series.

When determinations of the amount of paraffin are to be made, then it becomes necessary to specify with exactness what is to be called paraffin. The most definite property that can be made use of for this purpose is the melting point. For several reasons it is convenient to include under this name hydrocarbons of melting-point as low as 35°—40° C.

The method proposed by Zaloziecki for the determination of paraffin is the following:—The most volatile portions of the petroleum are separated by distillation, until the thermometer shows 200° C. These portions are separated, as they exert great solvent action upon paraffin. At the same time, he finds that no pyro-paraffin is formed under this temperature. A weighed portion of the residue is taken and mixed with ten parts by weight of amyl alcohol and ten parts of 75 per cent ethyl alcohol; the mixture is then chilled for twelve hours to 0° C. It is then filtered cold, washed first with a mixture of amyl and ethyl alcohols, and then with ethyl alcohol alone. The paraffin is transferred to a small porcelain evaporating dish and dried at 110° C. It is then heated with concentrated sulphuric-acid to 150°—160° C. for fifteen to thirty minutes with constant stirring. The acid is then neutralised and the paraffin extracted by petroleum ether. On evaporation of the solvent, the paraffin is dried at 100° C., and weighed. Zaloziecki found, according to this method, in three samples of Galician petroleums, 4·6, 5·8, and 6·5 per cent, respectively, of proto-paraffin. The method was carried out as above, with four samples of American petroleums, Colorado oil from Florence, Col.; Warren County oil from Wing Well, Warren, Pa.; Washington oil from Washington County, Pa.; Middle District oil from Butler County, Pa., all furnished by Professor Sadtler.

They were very different in physical properties and in appearance, the Colorado oil being a much heavier oil than the others, and the Washington oil being an amber oil, while the other two were of the ordinary dark green colour and consistence. The losses on distillation to 200° C. were very different, being about one-tenth in the case of the Colorado oil, and nearly one-half in the case of the others. The percentages of partially refined proto-paraffin in the four reduced oils (all below 200° C. off) were as follows:—For the Colorado oil, 23·9 per cent; for the Warren oil, 26·5 per cent; for the Washington oil, 26·6 per cent; and for the Middle District oil, 28·2 per cent.

The question now arises, what value has this determination of the proto-paraffin which may exist in an oil? As before said, a portion of the paraffin is always decomposed in distillation at temperatures sufficiently high to drive over the paraffin oils, so the yield of pyro-paraffin is always less than the proto-paraffin shown to be present originally. Zaloziecki found this in the case of the several Galician oils he examined. Corresponding to the 4·6, 5·8, and 6·5 per cent of proto-paraffin in the several oils, he obtained 2·18, 2·65, and 2·35 per cent, respectively of pyro-paraffin.

For the present, however, the extraction of proto-paraffin on a large scale by means of such solvents as amyl and ethyl alcohols is out of the question on account of their cost. A distillation, under reduced pressure and with superheated steam, would, however, prevent much of the decomposition of the original proto-paraffin and increase the yield of pyro-paraffin.

This study of Zaloziecki's method and the examination of American oils was suggested by Professor Sadtler, and carried out in his laboratory.

THE DETERMINATION OF SULPHURIC ACID IN PRESENCE OF IRON.

By P. JANNASCH and T. W. RICHARDS.

IT has long been known that the precipitation of barium sulphate in presence of iron salts gives very irregular results. As far back as 1877 Fresenius proposed to fuse pyrites with a mixture of sodium carbonate and potassium nitrate, and to determine the sulphuric acid in the filtrate from the watery extract of the melt. Lunge regarded this method as too complicated and tedious, and preferred to dissolve the mineral in nitro-hydrochloric acid, and to remove impurities from the precipitate by subsequent treatment with hydrochloric acid.

The authors, on a re-examination of the question, attempted to convert any ferric salts present into the ferrous state by reduction with sodium amalgam, metallic magnesium, or zinc. The results were so unsatisfactory

that this idea had to be abandoned. Iron was not absent in the precipitate, and the oxide of the reducing metal was also present.

Special experiments were made to decide if the presence of organic acids (citric, acetic, or formic) would prevent the precipitation of iron. The results were not satisfactory, and the barium sulphate obtained had the usual reddish tone. The error is in the first place a function of the iron simultaneously present, which falls out rather smaller with ferrous than with ferric salts. It was established that barium sulphate is not soluble in cold ferric solutions, and though somewhat soluble in hot ferric solutions it is re-deposited on cooling.

Attempts were made to remove the iron from the barium sulphate by digesting with hydrochloric acid before ignition. The precipitate was washed by decantation, digested for a considerable time with an excess of ammonium sulphide, and then treated with very dilute hydrochloric acid. The barium sulphate, however, had a reddish colour after ignition.

It appears that the iron is thrown down as a double compound with barium, barium-ferric sulphate, which is decomposed only at bright redness.

The experiments show that in presence of iron an accurate determination of sulphuric acid by direct precipitation with barium chloride is not practicable. For a correct analysis of pyrites the soda-nitre melting process of Fresenius is the only accurate method. The result of the titration of sulphuric acid in presence of iron with barium chloride must be abandoned, since the double iron-barium sulphate is thrown down, and too little barium chloride is consumed.—*Journal für Praktische Chemie*, New Series, vol. xxxix., p. 321.

ON THE

PREPARATION AND PROPERTIES OF METALLIC MANGANESE.*

By CHARLES BULLOCK.

The properties of manganese, like those of iron, appear to differ according to the method used in the reduction of the metal. When obtained from the oxide by heating with carbon, most authorities agree in the statement that the metal oxidises so readily in the air that it can be preserved only under "rock oil," or in well sealed vessels. In water it is said to "oxidise rapidly, with evolution of hydrogen, and crumbles into a dark grey powder."

Cast manganese containing eight per cent of iron is said to be unalterable in the air.

In the year 1869, some manganese prepared after the process of Brunner (the reduction of the chloride mixed with fluor-spar, by means of sodium) was found to have as little tendency to oxidation as iron.

Repeating recently this process, pure chloride of manganese was fused in a clay crucible and poured on a stone slab; when cold it was pulverised and mixed with an equal weight of powdered fluor-spar. This mixture, divided into portions of one ounce, was introduced into a French clay crucible, previously heated to redness. Eighty grains of sodium, cut into small pieces and freed from naphtha, being added to each portion, the crucible was covered, and reaction allowed to take place before adding another charge. After six ounces of the mixture had been added, the contents of the crucible was covered with fused chloride of sodium in powder, the cover replaced, and the heat carried to quiet fusion. After the flux became entirely fluid the heat was continued for ten minutes. The crucible was then removed from the fire, and, after cooling, the metal was found as a button at the bottom.

Three crucibles, of the capacity of eight fluid ounces each, were used at a time in a furnace without artificial blast. Care is necessary not to urge the heat too high, otherwise the crucibles will not resist the action of the fluor-spar flux. The French clay crucibles (Beaufay) were used on account of their greater freedom from iron and silica; they also resist the flux better than the Hessian, black-lead, or iron crucibles.

The yield of manganese under favourable circumstances was about twenty per cent of the chloride used.

Reduction was also tried by using fused chloride of sodium without fluor-spar, the yield of metal was much less, and differing in some of its properties from that obtained with the use of fluor-spar. Manganate of soda was formed when sodium chloride alone was used as a flux.

Manganese thus obtained is very brittle, with a steel white fracture, so hard that a file will scarcely touch it; the edges of the fractures scratch and almost cut glass.

The metal retains the brightness of a fractured surface after prolonged exposure to the air, and appears not more disposed to oxidation than iron. It is entirely passive to magnetic attraction.

The specific gravity of the metal obtained when fluor-spar was used was 7·072, when re-melted under fused sodium chloride the specific gravity rose to 7·153.

The metal obtained without the use of fluor-spar was less brittle, and had a different fracture; its sp. gr. was 7·231.

Authorities differ regarding the sp. gr. of manganese, ranging it from 6·85 to 8·013.

An examination of the metal obtained, using fluor-spar as a flux, showed the absence of iron and the presence of calcium, demonstrating the reduction of some of the latter metal from the spar. This may account in a measure for the increased sp. gr. on re-melting under sodium chloride, as also the greater sp. gr. of the metal when the spar was not used. As calcium has the sp. gr. of 1·57, a small amount alloyed with the manganese would sensibly affect its gravity.*

THE INFLUENCE OF SILICON ON THE DETERMINATION OF PHOSPHORUS IN IRON.†

By THOMAS M. DROWN, Professor of Analytical Chemistry in the Massachusetts Institute of Technology, Boston.

The process for determining phosphorus in iron now in most general use in the laboratories of iron and steel works is, I think, the one proposed by Mr. Emmerton.‡ In this process the solution of the iron for precipitation by ammonium molybdate is effected by treating the iron with nitric acid, evaporating to hard dryness in a dish, taking up with hydrochloric acid, and driving off the greater portion of the hydrochloric by nitric acid. This procedure accomplishes, first, the destruction of all the carbonaceous matters; and, second, renders all the silica insoluble.

Experience has proved the former—the complete oxidation of the carbon—to be absolutely essential; but the explanation usually given, namely, that unless the carbon compounds are destroyed they will have a solvent action on the yellow precipitate, I am inclined to doubt. It seems to me more probable, as suggested by Mr. P. W. Shimer, that the conditions which are favourable for the oxidation of the carbon compounds ensure the complete oxidation of the phosphorus to ortho-phosphoric acid, and that the reason of the imperfect precipitation of the phosphorus, when the solution of the iron in nitric acid is directly precipitated by molybdate solution, is that the phosphorus is not completely oxidised.

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* Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

* Sp. gr. of iron—gray, 7·1; white, 7·5; pure, 7·84.

† *Transactions of the American Institute of Mining Engineers*, vol. xviii.

‡ *Ibid*, xv., 93.

There have been many means proposed for destroying the carbon compounds—chromic acid, potassium chlorate, potassium permanganate, hydrogen peroxide, and others which accomplish the purpose without the necessity of evaporating the solution to dryness. The advantage of the latter method, however, has been supposed to be that in this way the silica was at the same time rendered insoluble.

The statement of Klein* that, in the determination of phosphoric acid in basic slag, it is not necessary to separate the silica, since the ammonium silico-molybdate is soluble in 3 per cent nitric acid, led me to try the effect of precipitating the phosphorus in a solution of pig-iron without previously evaporating to dryness. The results agreed perfectly with others obtained in the usual way after the removal of the silica; and further investigation showed that the silicon, at least in the form in which it exists when pig-iron is dissolved in nitric acid, is not precipitated by the molybdate solution.

There is a very marked difference in the effect of nitric acid of different strengths on pig-iron, as regards the condition of the silicon. When the acid is strong (1·2 to 1·4 sp. gr.) much of the silicon becomes gelatinous and prevents filtration, while with more dilute acid the silicon goes almost entirely into solution.

In a former communication to the Institute† I gave the effect of different strengths of hydrochloric acid on the silicon in pig-iron, showing that the strongest acid renders nearly all the silicon insoluble, and that weak acid dissolves it almost entirely. Generally speaking, the same is true, also, of nitric acid, as the following determinations show. It is interesting to note in the following figures that a nitric acid of medium strength dissolves more silicon than acid either stronger or weaker.

The pig-iron used in the following tests was a No. 1 foundry-iron, containing 2·42 per cent silicon.

Effect of Nitric Acid of Different Strengths on the Silicon in Pig-iron.

Acid. Sp. gr	Silicon, per cent. In graphitic residue.	Silicon, per cent. In solution.
1·4	2·28*a*	0·14
	2·01*a*	0·34
1·2	0·75*a*	1·67
	0·44*a*	1·98
1·16	0·07	—
	0·07	—
1·135	0·07	—
	0·06	—
	0·06	—
	0·06	
1·116	0·09	—
	0·11	—
1·102	0·12	
	0·12	—
	0·12	—
	0·12	—
	0·13	—
1·082	0·23	—
	0·23	—
	0·23	—
1·070	0·20	1·12
	0·24	—
	0·27	2·14
	0·31	2·12

a By difference.

The solutions obtained with the use of acid of 1·4 and 1·2 sp. gr. could not be filtered in concentrated condition, owing to the gelatinous form of the silica. They were, therefore, largely diluted, and an aliquot portion of the solution was obtained by filtration. In this the silicon was determined.

The solutions obtained with acid of 1·116 sp. gr., and still more dilute, can be filtered without difficulty,

The separation of gelatinous silica is not wholly a matter of strength of acid, neither is it wholly a matter of the percentage of silicon in the pig-iron. It has often been noted that different pig-irons, under identical treatment with nitric acid, will filter at different rates; and sometimes the iron with least silicon proves most refractory in filtering. This suggests that silicon may exist in different conditions in pig-iron, a subject which cannot be further discussed in this paper.

Another pig-iron was tested in this series of experiments—a grey forge iron, containing 0·63 per cent of silicon—with the following results:—

Silicon in Graphitic Residue.

	Per cent.
Acid, sp. gr. 1·2	0·19
	0·20
Acid, sp. gr. 1·135	0·03
	0·03
	0·05
	0·06

From the foregoing it will be seen that the strength of nitric acid most favourable for the solution of pig-iron is about 1·135 sp. gr., and not 1·2, which is generally used.* In the solution thus obtained there is no tendency of the silica to separate; not until the solution has been concentrated, by boiling to small bulk, does the silica begin to gelatinise.

When molybdate solution is added to a solution of pig-iron obtained in this way, the phosphorus, as might be expected, is but partially precipitated, because this treatment with nitric acid is insufficient to oxidise all the carbonaceous matter; or, as I prefer to believe, insufficient to oxidise all the phosphorus to ortho-phosphoric acid. To effect this object any of the oxidising agents already mentioned may be used. Potassium permanganate, as prepared by Shimer,† seems to me the most convenient; but for the solution of the separated manganese peroxide I use, instead of hydrochloric acid, a small quantity of some organic substance, such as tartaric, citric, or oxalic acid, or sugar. The manganese oxide disappears almost immediately on the addition of the organic matter. After this treatment, which requires only a minute or two, the molybdate solution will give a complete precipitation of the phosphorus.

The following determinations were made in order to discover whether there is any tendency for the silicon in solution to be carried down with the yellow precipitate, either mechanically or as silico-molybdate. The pig-iron used was that already mentioned, containing 2·42 per cent silicon.

Silicon determined.	I. P.c.	II. P.c.	III. P.c.	IV. P.c.
In residue from nitric acid solution	0·040	0·040	0·070	0·100
In yellow precipitate ..	0·030	0·050	0·012	0·012
In washings of the yellow precipitate with 2 per cent nitric acid	0·050	0·030	0·007	0·004
In filtrate from the yellow precipitate	2·250	2·210	2·340	2·280
Total	2·370	2·330	2·429	2·396

There seems to be, then, no evidence of the formation of any precipitate of ammonium silico-molybdate.

If the separation of the silica is omitted, the determination of phosphorus in pig-iron may be carried out in very much less time than is ordinarily required. In the laboratory of Massachusetts Institute of Technology we have adopted the following procedure:—About 1·5 grms. of the pig-iron (or more if very low in phosphorus) is treated in a covered beaker with 60 c.c. of nitric acid of 1·135 sp. gr. (If preferred, 20 c.c. of water may be first added, and then 40 c.c. of nitric acid, sp. gr. 1·2. In this variation the action is at first a little less violent). The

* *Chem. Zeitung*, x., 721.

† *Transactions of the American Institute of Mining Engineers*, viii., p. 514.

* Acid of 1·135 sp. gr. is conveniently made by diluting acid of 1·2 sp. gr. with half its bulk of water, or by diluting 1·4 sp. gr., and with water in the proportion of 3 to 7.

† *Transactions of the American Institute of Mining Engineers*, xvii.

beaker is heated on an iron plate until action ceases; three minutes is usually sufficient time if the borings are reasonably fine. The solution is then filtered from the graphite into a 500 c.c. flask, and to the boiling filtrate is added 15 c.c. of permanganate solution of 5 grms. to the litre.* Boiling is continued until the pink colour has disappeared, and a few very small fragments of tartaric acid are then added, causing the precipitated manganese peroxide to go almost immediately into solution. The amount of tartaric acid need not exceed 0·1 grm., although the addition of an excessive quantity—as much as 1 grm. —does not influence the results perceptibly. To the clear solution 10 c.c. of strong ammonia (sp. gr. 0·90) are added to partially neutralise the free nitric acid. This amount leaves the solution still amber-coloured; it should not be so far neutralised as to become wine-coloured. When the solution has cooled down to 90° C., 80 c.c. of molybdate solution† is added, and the flask is closed with a rubber stopper, wrapped in a towel and shaken vigorously for five minutes, as recommended by Emmerton. From this point on the directions of Emmerton, in his paper already mentioned, are followed, namely, reduction by zinc and titration by permanganate. If fine powdered zinc is used it may be entirely dissolved in about ten minutes, but filtration from the undissolved zinc seems generally to be preferred.

The following results were obtained in this way on the sample of pig-iron containing 2·42 per cent of silicon, in comparison with the older method of dissolving the iron in nitric acid, evaporating to dryness to separate silica, and precipitations by molybdate solution and magnesia mixture.

No. 1 Pig-iron containing 2·42 per cent Silicon.
Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.	By the New Method (Contd). Per cent.	Per cent.
0·284	0·272	0·297	0·286
	0·279	0·296	0·294
	0·290	0·289	0·294
	0·280	0·291	0·288
	0·291	0·291	0·292
	0·292	0·278	0·288
	0·289	0·294	
	0·292	0·293	

The rate of oxidation of the reduced molybdenum sesquioxide, on exposure to the air, is very slow, and is not ordinarily taken into account. Mr. J. W. Loveland found that it amounted, in this series of experiments, to 0·001 per cent of phosphorus for every ten minutes' standing before titration with permanganate. All the foregoing results have been corrected accordingly.

If rapidity of determination is of the first importance, a few minutes may be saved by omitting the filtering off of the graphite. Many trials show that this omission does not affect the accuracy of the results, although the removal of a foreign insoluble substance from the liquid enables one to carry out the process with greater satisfaction.

The following determinations of the phosphorus in the sample of gray-forge iron containing 0·63 per cent silicon were made without filtering off the graphite by Mr. Greeley, a student at the Massachusetts Institute of Technology.

Gray-forge Iron containing 0·63 per cent Silicon.
Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method, without filtering from graphite. Per cent.	Per cent.
0·632	0·620	0·627
0·635	0·625	0·629
	0·631	0·645
	0·640	0·635
	0·633	

Two determinations made in the solution of the same pig-iron, after filtering from the graphite, gave 0·636 and 0·631. Further results obtained by Mr. Greeley are given below:—

Bessemer Iron containing 1·18 per cent Silicon.
Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.
0·084	0·083
0·087	0·085
	0·086
	0·086
	0·085

No. 1 Pig-iron containing 2·29 per cent Silicon.
Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.
0·334	0·324
0·330	0·327
	0·334
	0·324
	0·322

The process for steel is, of course, the same as for pig-iron, except that the question of filtration from graphite does not arise.

In a sample of Bessemer steel the following percentages of phosphorus were obtained.

By the Old Method. Per cent.	By the New Method. Per cent.
0·061	0·064
	0·060
	0·061

By one familiar with the details of the process, a determination of phosphorus in pig-iron can be easily made in less than an hour.

I am indebted to Mr. James W. Loveland, Assistant in Chemical Analysis in the Institute of Technology, for valuable aid in this investigation; the credit for the analytical work, except as otherwise mentioned, is due entirely to him.

* The strength of this solution is not a matter of importance; I have found the above amount sufficient. Shimer uses 10 c.c. of a solution of 20 grms. to the litre.

† Made by dissolving 100 grms. of molybdic acid in 400 c.c. ammonia, sp. gr. 0·96, and adding 1000 c.c. nitric acid, sp. gr. 1·2.

NOTICES OF BOOKS.

The Metallurgy of Silver. A Practical Treatise on the Amalgamation, Roasting, and Lixiviation of Silver Ores, including the Assaying, Melting, and Refining of Silver Bullion. By M. Eissler, Mining Engineer and Metallurgical Chemist, formerly Assistant Assayer of the U.S. Mint, San Francisco. London: Crosby Lockwood and Son.

A short time ago we had the pleasure of noticing Mr. Eissler's excellent work on the metallurgy of gold, and we now welcome its companion treatise as equally practical, comprehensive, and trustworthy. The predominant, if not exclusively, American character of the author's experience is here no drawback, since in modern times an overwhelming excess of the world's supply of silver has been drawn from the Western Hemisphere. Asia and Africa—whatever may have been the case, *e.g.*, in the days of Solomon—scarcely figure as silver-producing regions at all. Australia yields an increasing supply, the ultimate extent of which is still problematical; whilst Europe furnishes about 14 per cent of the whole. Thus silver-mining with its accessory operations may be viewed substantially as American industries.

In the outset of the volume the author gives, from the eminent geologist Clarence King, a most instructive summary of the metallic deposits of Western North America.

The methods here considered for effecting the separation of silver from its ores are two, the amalgamation process —wet or dry—and lixiviation. Other methods, suitable for different classes of silver ores, will be discussed in a future work.

We are compelled to enter a protest against a misuse of language met with in the preface. Says Mr. Eissler (p. 6), "Of late years a new *science* has been developed in the treatment of silver ores which cannot be worked profitably by amalgamation, &c." That a new *art* has arisen is admitted, but a new *science* is inconceivable, unless some novel category of phenomena is detected which has hitherto escaped human observation, or unless man becomes endowed with a new sense.

The author takes up systematically the different processes, and describes them, not as a compiler from the writings of others, but from personal, prolonged, and extended observation. The Patio process, he considers, could not be profitably superseded by any other where labour is cheap, the ores are poor, and fuel, and even water-power, is scarce. The loss of mercury is its great drawback, and this is reduced at Guadelupe y Calvo by the use of copper amalgam.

The "Washoe process" is described as used on the Comstock lode. A brief mention is made of absurd ingredients added by unchemical operators to facilitate amalgamation. Among these figure tobacco-juice and decoction of sage-bush. Even the addition of copper sulphate and common salt is of doubtful benefit. In some mills both these ingredients are used, in others salt alone, and in others again, neither, and yet the results are described as equally good. The machinery used in crushing and amalgamating is clearly described and illustrated by a number of figures drawn to scale.

The fourth chapter gives a full conspectus of the cost and result of milling operations. The total cost of treating a ton of ore is given as £1 14s., but where water-power is available it may fall below £1. The loss of mercury is considerable. It is even carried by escaping steam to the roof of the mill. If contaminated with copper it becomes coated with iron. It is also coated with iron pyrites, grease, and slimes. As a cleansing agent potassium cyanide is recommended. Ores containing talc have an unfavourable effect on the mercury. Manganese dioxide is a most objectionable ingredient of ores, occasioning heavy loss of quicksilver.

Chapter V. gives an account of the treatment of slimes and tailings, an important subject, as they sometimes contain a very considerable proportion of silver.

The dry process is next followed through its several stages of chlorinising, roasting, and amalgamation, and the necessary plant is duly figured.

The treatment of silver ores by lixiviation forms the subject of Chapter XIII. The modifications devised by Augustin, Ziervogel, and Russell are duly described. The comparative advantages of this modification as compared with amalgamation are fully explained. It requires a cheaper plant, it requires less mechanical power, saves the capital locked up in the stock of mercury, extracts a much higher proportion of silver, and, unlike amalgamation, it does not interfere with the health of the workmen.

The last chapter is devoted to the operations of assaying by the dry and the wet method, and refining. For bullion, alloys, &c., the author decidedly prefers the Gay-Lussac (volumetric) assay. He remarks that should appreciable quantities of non-oxidisable metals be present the dry assay is not available.

To all persons connected with or interested in the metallurgy of silver, this work will prove indeed a boon, giving, as it does, an account of all the most recent improvements by a writer who thoroughly understands his subject.

Inorganic Chemistry. By Ira Remsen, Professor of Chemistry in the Johns Hopkins University. London Macmillan and Co.

As regards its extent and scope, this work occupies a medium rank between those short manuals or cram-books which have been produced of late years in such alarming numbers, and the encyclopædic treatises of Gmelin, Watts, or Roscoe and Schlorlemmer. As a favourable feature, we most notice that Prof. Remsen has not arranged his teaching to suit any "syllabus," nor does he address himself specially to students preparing for some examination. Neither does he furnish lists of papers which have been set, or questions which have been put by any college or department. He aims at teaching chemistry, leaving it to his readers to apply the facts and the laws laid down to any particular purpose required A peculiarity of the work, which, upon the whole, may be called advantageous, is that the experiments used in illustration and the apparatus needed for their performance are described and figured, not in the text, but in an appendix.

The classification of the elements has been carried out in accordance with the periodic system. In speaking of this system, the author certainly admits the priority of Mr. J. A. R. Newlands, but he seems to us to underrate his share in the discovery. He writes:—"Newlands's arrangement was quite imperfect." We can of course understand a system or an arrangement being "quite perfect" or "very imperfect," but we fail to see how a relative attribute, such as imperfection, can be qualified by any word which implies absoluteness.

We are pleased to find that Prof. Remsen recognises that the two departments of chemistry commonly known as the static and the dynamic or kinetic, bear to each other relations similar to those existing between morphology and physiology.

The author does not enlarge on questions which are as yet under investigation. On the possible origin and relations of the elements he is silent, accepting them as ultimate in the light of our present knowledge.

Although the work deals mainly with general principles, the practical and technical applications are by no means overlooked. The author's remarks on the waters of rivers, when used for domestic purposes, are exceedingly good, and show a judicious avoidance of extreme views. He writes:—"River-water, when once contaminated by drainage, tends to become pure again by contact with the air. . . . If the water is to be used for drinking purposes, however, it is not well to rely too much upon this process of purification. So much attention has of late years been given to the subject of drinking-water, that water is no doubt frequently held responsible for sickness with which it has little or nothing to do. In some places the war against the water-supply has been carried so far that those who can afford it drink only artificially purified and distilled water. It is undoubtedly well to be cautious, but it is possible to be too cautious." Prof. Remsen admits that chemical analysis cannot, in all cases, detect minute traces of extremely injurious substances.

Generally speaking it may be said that whoever wishes to obtain a correct and clear view of the principles of chemical science without entering into minute details will find this work admirably suited to his purpose.

An Elementary Treatise on Heat. By H. G. Madan, M.A., F.C.S. London: Rivingtons.

In his preface the author recommends a study of the phenomena and the laws of heat as "a very suitable and fruitful subject for school instruction." Very justly he recommends such instruction to be given to boys before they proceed to the more difficult study of chemistry. In justification of the expression "more difficult" he drily adds, in a note:—"If, that is, the subject is to be treated in a really scientific spirit, and not merely as an excuse

for producing brilliant effects of light and colour, startling explosions, and unsavoury smells." He declares that the laws of heat seem worthy of better treatment than to be considered as little more than subjects upon which arithmetical questions may be set for the purposes of a competitive examination (after the manner of numerous text-books of the present day)." Here, indeed, is a danger connected with the introduction of numerical exercises in courses of instruction in any branch of physical or natural science—that they are made to play into the hands of the examinational system, and to divert the mind of the student from the most important lessons which such studies ought to impart. The author employs, indeed, mathematical formulæ, but "only after a full statement in ordinary language of the facts which they express." In speaking of experiments before a juvenile auditory he gives a needful caution. "The work of science-lecturers often seems to be little more than a perpetual struggle against the malice of nature. Not a few interesting experiments have to be omitted, even by skilled lecturers, as too tedious or too uncertain for the conditions of a lecture-room. Here he adds a footnote which is too good not to be reproduced. M. Regnault was once asked by an eminent English chemist how he succeeded in the manipulation of a certain experiment which was very graphically described in his 'Cours Elémentaire de Chimie.' He replied:—'*Monsieur, c'est une expérience qu'on ne fait pas.*'"

After an introductory chapter the author discusses the nature of heat, its sources, natural and artificial, its effects upon substances, the measurement of temperature, the measurement of quantity of heat, the phenomena connected with change of state, the transmission of heat by conduction, convection, and radiation, the relations between heat and mechanical motion, and heat-engines. In conclusion we find a notice of the depreciation—commonly called "degradation"—of energy. Heat, unfortunately, is the socialist of the physical world, always seeking to run down to a dead level, and so far we have not been able to convert heat into other forms of energy without very great loss. Mr. Madan happily compares heat to a security in the money market, "which, though its intrinsic value may be great, yet cannot be converted into cash except at a ruinous loss, and is therefore depreciated in value." We do not know an elementary work on heat which we could recommend as preferable to the one before us.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 24, June 17, 1889.

The Combustion and Formation Heats of the Nitrites.—MM. Berthelot and Petit.—The authors consider the nitrites as the type of the compounds, capable of furnishing heat by simple hydratation over and above any phenomenon of oxidation. This result they consider very important as regards animal heat. The values due to hydratation exceed one-third of the combustion heat of the carbon contained in the organic compound.

The Thermo-chemical Method Summarised in its Principles and Results.—M. Sappey.—This is not a chemical paper, but the explanation of a method proposed for microscopic anatomical research.

On a New Method of Preparing the Alkaline Nitrates.—G. A. Le Roy.—The usual means of preparing these nitrites are the decomposition of the corresponding nitrates by a limited heat, their partial deoxidation by perfectly oxidisable bodies, such as graphite, reduced copper or lead (dry way) zinc powder, finely divided lead (moist way), alkaline sulphites, &c. The author's novel method is to cause two mols. of the alkaline nitrate to react with one mol. barium sulphide. The sulphide is reduced to a fine powder, intimately mixed with the nitrate, and the mixture is projected with constant stirring into an iron basin kept at dark redness. The reaction takes place with incandescence. The resulting mass is extracted with water. The presence of large doses of barium sulphate in the sulphide moderates advantageously the reaction by preventing the too rapid decomposition of the nitrate.

The Action of the Diamines upon the Diacetones.—M. Alphonse Combes.—This paper is not adapted for useful abstraction.

On Crystalline Tanghinine Extracted from the Tanghinia Venenifera of Madagascar.—M. Arnaud.—This poisonous principle is concentrated in the kernel of the fruit of an Apocyeous tree. The oily matter, which forms about 75 per cent of the kernel, is perfectly harmless. Tanghinine is a heart-poison, approximating to strophantine and ouabaïne, but, unlike these two, it has a general convulsive action. From 2·550 kilos. of the kernels the author obtains 25 grms. of pure crystalline tanghinine. It is colourless, and crystallises in rhombs from its alcoholic solution. It is anhydrous, and gives no coloured reactions. It melts at 182° to a transparent liquid, and if heated more strongly it burns without any residue. It is very sparingly soluble in water, moderately soluble in ether, and freely soluble in strong alcohol. It deflects the plane of polarised light to the left. If heated with dilute acids it is decomposed, yielding a yellowish resinous product. No reductive sugars are formed, such as are obtained from ouabaïne, strophantine, and the other glucosides. It contains rather more carbon than ouabaïne and strophantine, but like the two latter, no nitrogen. It is therefore neither an alkaloid nor a glucoside.

The Expansion of the Spectral Rays of the Metals.—M. Gouy.—(See p. 5).

Colloid Cellulose, Soluble and Insoluble; Constitution of Parchment Paper.—C. E. Guignet.—Dry cellulose in contact with sulphuric acid at 50° B., if the temperature is not allowed to rise, is converted into a transparent gelatinous mass. At 100°, or even below that point, it is quickly converted into dextrine. After being completely washed, colloid cellulose dissolves in pure water. The solution is precipitated by very small quantities of sulphuric or nitric acid, sodium chloride, or sulphate-lead acetate, &c. Vegetable parchment is a tissue of ordinary cellulose, the pores of which are filled up with colloid cellulose.

No. 25, June 24, 1889.

The Condition of Matter near its Critical Point.—L. Cailletet and E. Colardeau.—The authors conclude that the critical temperature of a liquefied gas is not that where the liquid evaporates totally and abruptly in the containing space. The liquid state persists beyond this temperature. Neither is it the temperature at which a liquid and its saturated vapour have the same density. It is the temperature at which a liquid and the gaseous atmosphere above it become capable of mutual solution in all proportions, forming, after ignition, a homogeneous mixture.

The Formation-Heat of the Hyponitrites.—M. Berthelot.—The author finds that the formation of hyponitrous acid takes place with a considerable absorption of heat.

The Occlusion of Gases in the Electrolysis of Copper Sulphate.—A. Soret.—Electrolytic copper contains only two gases, one of which, hydrogen, is generally

in excess, always, indeed, if the electrolyte is acid. The fragility of the deposits is correlated with the presence of carbonic acid in excess.

The Ammoniacal Compounds of Ruthenium.—A. Joly.—The salts of the ammoniacal ruthenium bases do not correspond to any of the salts of the ammoniacal bases of the other platinum metals. Jörgensen, who has made an elaborate study of the ammoniacal rhodium compounds, has indicated the relations of isomorphism, connecting them to the ammoniacal compounds of cobalt and chrome, discovered by Fremy. Here we can find nothing similar; at the utmost the ruthen-ammonium salts may be approximated to the fusco-cobaltic salts.

Researches on the Hyponitrites.—M. Maquenne.—The author describes the silver, barium, ethyl, calcium, and strontium hyponitrites, and the calcium, strontium, and barium acetohyponitrites. He concludes that nitrous oxide cannot be the anhydride of hyponitrous acid.

The Presence of Sodium Sulphate in the Atmosphere and the Origin of Saline Dust.—P. Marguerite-Delacharlonny.—The author considers that every soluble salt contained in waters and in the soil must be carried away by the evaporation of its solution, and must be found in small quantities in the air.

The Camphor and the Borneol of Rosemary. New Method of Separating Camphor and Borneol.—A. Haller.—The camphor of rosemary is a mixture of dextro-camphor and borneol, and of laevo-camphor and borneol. In order to separate camphor and borneol, the author triturates 200 grms. of the sample with about 120 grms. of pulverised succinic acid, and heats the mixture for forty-eight hours in flasks to about 140°. When the flasks are withdrawn from the oil-bath the contents separate into two layers: the one, solid and crystalline, consists of succinic acid; the other, a yellowish liquid, floats at the top, and contains a combination of succinic acid with borneol and also the camphor. The whole is then treated with ether, which dissolves the camphor and the acid borneol succinate, whilst the succinic acid remains insoluble. The ethereal liquid, after being repeatedly agitated with a solution of sodium carbonate, deposits the acid borneol succinate, whilst the camphor remains dissolved.

Zeitschrift fur Physikalische Chemie.
Vol. iii., Part 2.

Evaporation and Dissociation. The Continuous Transition from the Gasiform to the Liquid Condition at all Temperatures.—W. Ramsay and Sydney Young.—The substance of this memoir will be found in the *Philosophical Magazine* for 1887, p. 196.

Evaporation and Dissociation. A Study of the Thermic Properties of a Mixture of Ethylic Alcohol and Ether.—W. Ramsay and Sydney Young.—From the *Journal of the Chemical Society*, 1887, p. 755.

The Molecular Weight of Nitrogen Dioxide.—W. Ramsay.—According to the results of five experiments the molecular weight of this compound is 92, and its formula N_2O_4.

Remarks on H. Biltz's Memoir on the Molecular Magnitude of Sulphur.—W. Ramsay.—The author considers it not disproved that sulphur exists as S_6. Biltz's experiments merely give room to the conjecture that there may possibly exist more complicated molecules, such as S_8 or S_{10}.

The Absorption of Hydrogen by Metals.—Dr. Max Thoma.—The author's chief results are:—1. The increase of palladium in bulk, when charged electrolytically with hydrogen, takes place equally in all directions. 2. The contractions on discharge by the development of oxygen become smaller with the number of charges, but show no regularity. 3. Palladium can absorb permanently only a certain quantity of hydrogen. Any proportion of hydrogen taken up in excess is spontaneously liberated. 4. Below this limit of saturation the expansion of palladium and of the alloy of palladium and platinum are proportional to the quantities taken up. 5. The absorption of hydrogen by palladium and by the alloy above the limit of saturation, is attended with expansion, and its spontaneous elimination with contraction. 6. In palladium the expansion by supersaturation is equal to the contraction on the spontaneous escape of hydrogen. 7. To each strength of current there corresponds a certain degree of supersaturation which cannot be raised by protracted electrolysis. 8. Probably with the supersaturation, reached at any given strength of current, there occurs a stationary condition, in which as much hydrogen penetrates into the cathode per second as there is set free in the same time. 9. After the limit of saturation has been exceeded the volume of palladium increases more rapidly for an equal absorption of hydrogen than corresponds to a similar absorption below the limit. Hence in supersaturated palladium the hydrogen exists in a far lower density than it does in palladium below the limit of saturation. 10. Hydrogen diffuses itself in palladium wire in the course of half an hour to a distance of 4—5 m.m. from the point of the wire exposed to electrolysis. 11. In the supersaturated state both palladium and its platinum alloy show a far greater hydrogen polarisation than in the saturated state. 12. Iron, as well as palladium, can be supersaturated with hydrogen, so that the gas is spontaneously eliminated. 13. This supersaturation occurs when iron comes in contact with dissociated hydrogen in the voltameter or on the action of acid upon the iron, but not when the iron is exposed to free hydrogen. 14. In iron a certain degree of supersaturation corresponds to every strength of the current. 15. The quantities of hydrogen spontaneously evolved from supersaturated iron are proportional to the surfaces of the charged iron.

Isotonic Coefficients of Certain Salts.—Hugo de Vries.—The salts examined are urea, magnesium sulphate, potassium, lithium, ammonium, calcium, magnesium, and strontium chlorides, calcium nitrate, and potassium ferrocyanide.

A Simple Diffusion Experiment.—W. Beyerinck.—This paper requires the accompanying woodcut.

On Raoult's Law of the Depression of Freezing-Points.—J. F. Eykman.—The numbers found experimentally range around the theoretical value, so that the author considered further determinations superfluous.

Simple Derivation of Relation Between Osmotic Pressure and Depression of Vapour Tension.—S. Arrhenius.—This memoir requires the two accompanying woodcuts.

On Free Ions.—W. Ostwald and W. Nernst.—This memoir does not admit of brief reproduction.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Thiocamf.—(Reply to G. E. Wright)—The thiocamf disinfectant may be purchased from the Thiocamf Disinfectant Company, 5, Lower Merrion Street, Dublin.—E. A. Werner.

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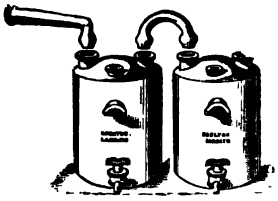

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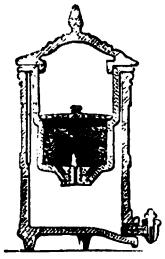

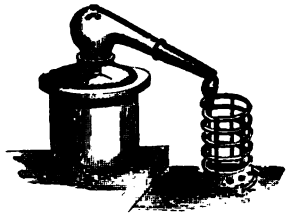

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London: Printed and Published for the Proprietor by Edwin John Davey, at the Office, Bell Court, Ludgate Hill, E.C.
July 12, 1889.

THE CHEMICAL NEWS.

Vol. LX. No. 1547.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

If I name the Spectroscope as the most important scientific invention of the latter half of this century, I shall not fear to be accused of exaggeration. Photography has rendered vast services in recording astronomical and biological phenomena, and it even supplies us with indirect means of studying ray vibrations to which the human retina does not respond. The electro-acoustic devices of Edison and his co-workers permit almost magical communication between human beings. Ruhmkorff's coil and the Geissler tube have rendered notable service in physical investigation; and the electric lamp promises to aid in exploring the internal parts of living animals, as well as in studying the organic forms of the deep sea. But in the spectroscope we possess a power that enables us to peer into the very heart of Nature. In the extent of its grasp and the varied character of its applicability it surpasses the telescope and at least rivals the microscope. It enables the astronomer to defy immeasurable distance, and to study the physical condition and the chemical composition of the sun and the stars as if they were within touch, and even to ascertain the direction of their movements.

Without attempting to discuss the import of the results thus gained—which would lead us too far—I may point out that they overthrow a dogma concerning the classification of the sciences. It has been said that the simpler and more general sciences lend both doctrines and methods to the more complex and less general sciences, and that the latter give nothing in return. But we now see chemistry endowing astronomy with an original and fruitful method of research.

Turning to the very opposite extremity of the scientific hierarchy we find that to the biologist the spectroscope is of value in studying the relations of animal and vegetable fluids, and even of certain tissues. But this wonderful instrument is clearly destined to play its chief part in what is called terrestrial chemistry—the field where it has won the most signal triumphs.

It must be remarked, despite this vast range of applicability, a range sweeping through the whole universe and embracing all the four elements of antiquity; and despite the astonishing results already achieved and the prospect of greater revelations to come, that the spectroscope is still inadequately appreciated by professed men of science, and in consequence is, to a great extent, ignored by the "educated and intelligent public." In urging its more thorough recognition I do not advocate the formation of spectroscopic societies for the fragmentary study of everything that can be observed with a spectroscope. But I recommend researching chemists to appeal to this instrument wherever requisite and possible.

An elaborate spectroscopic study of the basic constituents of rare minerals from different localities would be of great value, and I would suggest that on all possible occasions meteorites should be submitted to careful spectroscopic analysis.

I do not propose to discuss all the splendid achievements of the spectroscope in chemistry; nor its applications in ordinary analysis, qualitative and quantitative; nor the conduct of technical operations, such as the Bessemer process. I confine myself to the light thrown by the spectroscope upon the nature and the relations of our *elements*, real or supposed.

Though systematically employed by few experimentalists, the spectroscope has already led to the discovery of several hitherto unknown elements. In the early days of spectrum analysis attention was mainly concentrated on the flame spectra: that is, the bodies in question were vaporised and rendered luminous by the action of a flame, such as that of the Bunsen burner or of the oxyhydrogen jet. This procedure in the hands of Bunsen and Kirchhoff gave us cæsium and rubidium; afterwards, in my own hands, thallium; and in those of Reich and Richter, indium.

Then followed the production and examination of spark-spectra. The spark produced by means of the induction coil, especially when its energy is reinforced by the intercalation of a Leyden jar, volatilises and renders luminous minute portions of matter, solid, liquid, or gaseous, which may then be examined by the spectroscope. In this manner gallium was discovered in 1875 by Lecoq de Boisbaudran. In consequence of the sharpness and the well-marked character of these spark-spectra they are relied on by chemists as certain proof of the identity of any two elements which yield identical spectra.

Next was introduced the systematic study of the absorption-spectra seen when a beam of light is passed through certain transparent solids or through solutions of various substances. One of the earliest observers in this branch of spectroscopy was Dr. Gladstone, who, in 1858, read before this Society a paper on the absorption of light by various metallic salts, and gave the first description of the absorption-spectrum of didymium. This branch of spectroscopy has proved not less fruitful in the recognition of new metallic elements.

In the investigation of the rare earths my principal object has been to separate the true from the undemonstrated and spurious, verifying the true, rejecting the spurious, and reducing as far as possible the number of the doubtful. In the following table I have given a list of the so-called "rare-elements," with which for the last seven or eight years I have been specially occupied. Column 1 gives the names by which they are commonly known. Column 2 gives their atomic weights, &c. Column 3 shows in what manner they come under the domain of spectroscopy; and columns 4 and 5 notify the components or meta-elements into which some of these bodies have been decomposed in 1886 by myself, and in 1887 by Krüss and Nilson. In the first column I have exercised a judicial leniency in retaining candidates, for the sake possibly of old associations, when strict justice would have disestablished them. Thus, it may be doubted whether decipium, philippium, or gadolinium should have been retained. But since doubts have been cast on the integrity of nearly all the occupants of this column the line should not be drawn too strictly.

At first spectroscopic examination was applied directly to substances, natural or artificial, which had not undergone any special preparation. The idea next occurred of attempting to split up substances supposed to be simple into heterogeneous constituents before appealing to the spectroscope. The refined chemical processes used for this operation may be summarised under the name of fractionation, whether they be fractional precipitations, crystallisations, or decompositions. The essential principles of this processes were so fully discussed on the last occasion when I had the honour of addressing you that I need not further allude to them.

The Didymium Group.

A combination of such delicate and prolonged chemical

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

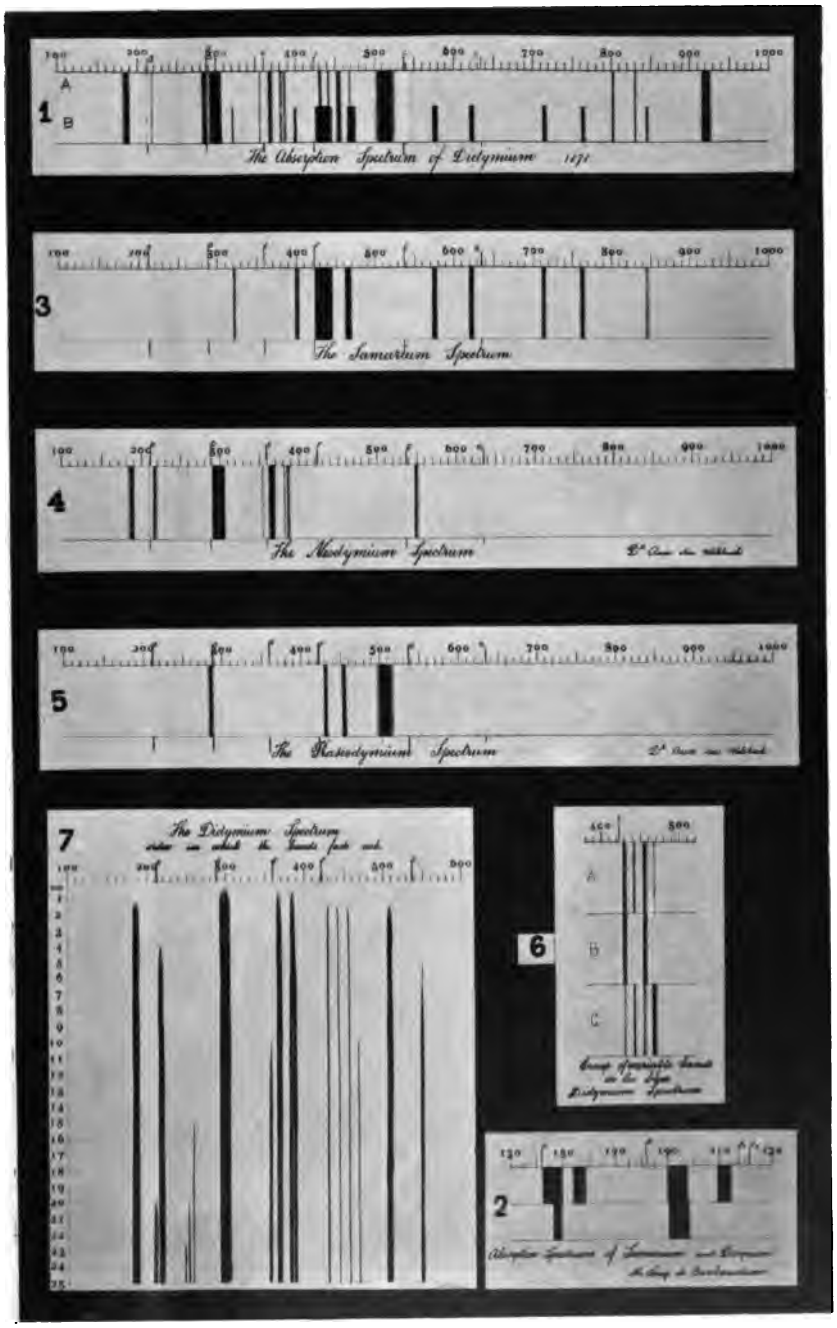
TABLE I.

	Atomic weight of Metal and Formula of Oxide.	Gives Spectrum by—	Component Meta-Elements according to— Crookes (1886).	Nilson and Krüss (1887).
Didymium ..	Neodymium— 140·3, Nd_2O_3. Praseodymium— 143·6, Pr_2O_3. Unnamed.	Absorption.	Dα λ=475	Diα Diβ Diγ Diδ Diε Diη Diθ Diι Diχ
Decipium				
Samarium ..	150·12, Sm_2O_3.	Absorption and phosphorescence.	Sδ Gε Gγ Gθ	Smα Smβ
Lanthanum ..	138, La_2O_3.	Phosphorescence.		
Erbium	166, Er_2O_3.	Absorption. and phosphorescence.	λ 550 λ 493	Erα Erβ
Philippium ..	45—48, PpO.	Phosphorescence.		
Holmium		Absorption.		Xα Xβ Xγ Xδ
Thulium	170·7, Tm_2O_3.	Absorption.		Tmα Tmβ
Dysprosium ..		Absorption.	λ 457—448 (1888)	Xζ Xε Xη
Yttrium	88·9, Yt_2O_3.	Phosphorescence.	Gα Gβ Gδ Gζ Gη	Zα Tb Yt (Lecoq de Boisbaudran.)
Terbium	124·7, Tb_2O_3.			
Gadolinium (Yα)		Phosphorescence.	Gβ Gζ	
Ytterbium ..	173·01, Yb_2O_3.	Phosphorescence.		
Scandium ..	44·03, Sc_2O_3.			

processes with spectroscopic examination applied to bodies showing absorption spectra soon led to important discoveries. Fig. 1A* shows what I may call the normal didymium spectrum, as it was generally recognised down to the year 1878. Fig. 1B shows the whole of the absorption-bands belonging to bodies subsequently separated from didymium by fractionation. When in 1878 the didymium from samarskite was examined by Delafontaine (*Compt. Rend.*, lxxxvii., 632; CHEM. NEWS, xxxviii., 223) he found it to differ somewhat from ordinary didymium as extracted from cerite and gadolinite, and by a series of chemical fractionations he succeeded in separating from it an earth which he called decipium, giving at least three absorption-bands, one having a wave-length of 416 ($1/\lambda^2$ 578); another narrower and stronger, at wave-length 478 ($1/\lambda^2$ 438), and a very faint "minimum of transmission" near the limit of the blue and green. Nine months later Lecoq de Boisbaudran (*Compt. Rend.*, lxxxix., 212; CHEM. NEWS, xl., 99) announced the discovery of samarium as a constituent of the didymium from samarskite, giving a drawing of the decipium and samarium spectra to a common scale (Fig. 2), from which it is seen that samarium is characterised by the bands of Delafontaine's decipium together with two additional bands. Fig. 3 shows the samarium spectrum from the latest measurements.

Still didymium was not reduced to its ultimate simplicity. In 1885 Carl Auer (*Monatsh. Chem.*, vi., 477), by fractionally crystallising the mixed nitrates of ammonium, didymium, and lanthanum, showed it was thus possible to cleave didymium in a certain direction and separate it into two other bodies, one giving green salts and the other pink salts. Each of these has a characteristic absorption spectrum, the sum of the two sets of bands approximating to the old didymium spectrum. These bodies the discoverer has named respectively praseodymium and neodymium. The neodymium spectrum (Fig. 4), according to Auer, consists of the whole of the bands in the red, with part of the large one in the yellow; it then misses all the green and blue, and takes in the second line in the violet. Fig. 5 is the spectrum of praseodymium, which I have also taken from Auer's description;

* All the figures are drawn to the $1/\lambda^2$ scale.



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.

W. CROOKES.

it takes the other part of the yellow band, and all the green and blue, except the second blue, which belongs to neodymium. Subtracting these two spectra from the old didymium spectrum (Fig. 1) you see there are still two bands left at λ 462 and 475 (1/λ² 465 and 443). Assuming that the argument from absorption-spectra is a legitimate one—and all recent research tends to show that if not quite trustworthy it is at all events a weighty one—the inference I draw from these results is that the old didymium still contains a third body distinct from neo- and praseodymium, to which one or both of these extra bands is due.

I must venture to lay especial emphasis on the words *in a certain direction*. Didymium in my own laboratory has undergone other cleavages, and I have not yet decided whether we shall have to recognise further decompositions of neodymium and praseodymium, or whether the original didymium is capable of being resolved differently according to the manner in which it is treated. Keeping the band in the orange always of the same strength, in many of the fractions of didymium from different sources the other bands of neo- and praseodymium are seen to vary from very strong almost to obliteration (Chem. News, liv., 27). In this way I have worked on the spectra of didymium from allanite, cerite, euxenite, fluocerite, gadolinite, hielmite, samarskite, yttrotitanite, &c., and the further I carry the examination the more the conclusion is forced upon me that didymium must not be regarded as compounded of two elements only, but rather as an aggregation of many closely allied bodies. Later researches of Krüss and Nilson have led them to the same conclusion.

When working in 1886 on the decomposition of the nitrate of didymium by heat, I found very decided indications of the possibility of depriving didymium of band after band until only the deep line in the blue λ 443 (1/λ² 509·6) is left (*Proc. Roy. Soc.*, xl., 503). I have provisionally named this single band element Dα. In this connection I would like to draw your attention to a few facts which have very recently come to light.

In some of my fractions of didymium the band λ 475 (1/λ² 443) intensifies in company with another band at λ 462 (1/λ² 465). Fig. 6 shows at A the group of blue bands as they are seen in a strong solution of didymium. It forms a well-marked set of four comparatively sharp lines, one at λ 462 (1/λ² 465) being the faintest. Under these lines I show (Fig. 6, B) the same group as seen in fractions of the same solution of didymium after disintegration has commenced. This fraction is very similar to Auer's praseodymium; and below this (Fig. 6, C) I again show the same group as seen in the didymium fractions most removed from the one last described. Here the two lines λ 475 (1/λ² 443) and λ 462 (1/λ² 465) have become very strong, while the other two have almost faded out. One of these, λ 475 (1/λ² 443), is included by Auer in the spectrum of his crude didymium, but he makes no further reference to it either in description or diagram. Of these lines, λ 462 (1/λ² 645), probably belongs to the samarium group, but the other, λ 475 (1/λ² 453), cannot belong to samarium, although it superposes on the most refrangible half of the broad and ill-defined samarium band.

In a paper read before the Royal Society dated June 9, 1886 (*Compt. Rend.*, cii., 1551), I gave an account of some observations I had made upon the line λ 475 (1/λ² 443), proving that it could be separated from the old didymium spectrum, and in conclusion said it "must be regarded as characteristic of a new body."

Subsequent to my paper Demarçay (*Ibid.*) drew attention to this line at λ 475 (1/λ² 443), and in 1887 (*Compt. Rend.*, civ., 580) he again returned to the subject, associating the two lines λ 475 (1/λ² 443) and λ 462 (1/λ² 465) as being due to the same element. With this opinion I cannot yet agree, for in many instances I have had fractions in which the relative intensities of the two are widely different. More recently Krüss and Nilson have ascribed this line to one of the constituents of Soret's X or holmium, which gives a line falling nearly on the same place (Chem. News, lvi., 154, 173).

By examining the absorption-spectra of solutions of rare earths obtained from widely different sources, Krüss and Nilson (*Ber.*, xx., Part xii., 2134; and Chem. News, lvi., 74, 85, 135, 145, 154, 165, 172) came to the conclusion that the elements giving absorption-spectra, and known as didymium, samarium, holmium, thulium, erbium, and dysprosium, were not homogeneous, but that each one contained almost as many separate components as it produced bands of absorption.

They have discovered that in didymium obtained from some minerals one of the fainter lines of the normal didymium spectrum is strong, while others usually stronger are almost or quite absent; results to which I shall presently refer will show that this cannot be explained by dilution or concentration. In this way, by examining a great number of minerals, they found anomalies occurred in the case of almost each of the old didymium lines, and therefore decided, as above mentioned, that it is a compound body, capable of resolution into at least nine separate components.

Identical arguments are brought forward to prove that each of the other so-called elements, samarium, erbium, holmium, thulium, dysprosium, &c., are compounds of many closely allied bodies.

Krüss and Nilson, I believe, are pushing their investigations with the object of isolating the separate components of these different earths. They, however, question the possibility of resolving the erbia and didymia earths into their several ultimate constituents by a fractionated decomposition of the nitrates. In fact they assert that by means of the methods of separation at present known it would be almost impossible to completely isolate any single constituent of the mixed earths. They therefore propose, as I had previously done,* a method by which we may certainly arrive nearer to the mark and dispense with much tedious fractionation. If we examine the minerals which contain these rare earths we find they occur in very different states of mixture or combination. Sometimes many of the constituents which we wish to separate are conjointly present, and sometimes but few. The desired differentiation, in fact, has already been commenced by Nature. Krüss and Nilson, therefore, whichever ingredient they wish to separate, propose to operate on a mineral which contains that ingredient as far as possible in a state of isolation. In other words, they will take advantage of the work that Nature has already begun, and endeavour by refined chemical means to put the last finishing touches to her work. Thus they will be able to work with smaller quantities of primary material,—no small consideration in the case of some minerals,—and to obtain results in a shorter time. How widely the composition of one and the same mineral, as judged by our searching physical tests, may vary, will be seem from the following instances. Fergusonite from Arendal shows six of the bands of holmium, fergusonite from Ytterby four, and that from Hitterö only three. Moreover, the ingredient provisionally called Xα is to be found in the fergusonite from Ytterby, but not in that of Arendal and Hitterö.

The foundation for thus firmly declaring what I had previously ventured to infer, is the striking differences in the spectra given by several specimens of one earth, say didymium, when obtained from different sources.

We are anxiously waiting the results of this investigation, but although the paper quoted was published in July, 1887, no further communication has come from these illustrious workers.

Chemists recently have stated as proof of the existence of new elements the fact that certain bands of absorption, as seen in various fractions, "follow the same variations of intensity." Before deciding the question whether

* "Address to the Chemical Section of the British Association, Birmingham Meeting," Chem. News, liv., 123. "On the Fractionation of Yttria," Chem. News, liv., 157. *Proc. Roy. Soc.*, xl., 1886. 505

didymium is a homogeneous whole, or whether an argument in favour of its heterogeneity can be based on the fact that the absorption spectra of didymium from different minerals differ *inter se*, it was necessary to ascertain if the absorption-bands seen in its solutions, whatever the thickness of the layer, whether dilute or concentrated, followed the same variations, and also to ascertain the nature of these variations. To contribute to this inquiry I examined the absorption-spectrum of a solution of neutral didymium nitrate containing one part by weight of metal in 10 of water, as seen through a series of cells from 1 m.m. to 25 m.m. in thickness. For this work I used a new form of binocular spectroscope, fitted with a mechanical tracing arrangement, so that each spectrum can be automatically mapped on paper strips; from this set of tracings I have arranged the diagram (Fig. 7) now before you. It represents the bands of the normal didymium spectrum. The figures running up the side represent the thickness of the layer of solution observed, and they show at a glance the "life" of each of the bands. At the bottom, 25 m.m. thickness, all the known bands are visible, and they become fainter and die out in the particular order here given, some of them remaining visible almost to the end. For instance, almost as long as the deep line in the blue part of the spectrum at λ 443 ($1/\lambda^2$ 509), my Da, can be distinguished, it is possible to see the group of three very narrow ones next to it. Two or three other less characteristic bands can be seen only when there is a very considerable depth of liquid; thus, the three lines in the red λ 636, 628, 622 ($1/\lambda^2$ 247, 253, 258), cannot be seen distinctly through less than 20 m.m. of this strength of solution.

Having ascertained in this series how the spectra varied in appearance with different thicknesses of the same solution (strength 1 of Di in 10 of water), I repeated the experiments, keeping the thickness of layer of solution constant, and diluting the standard solution of didymium so that the rays of light passed through the same quantity of metal as in the former series. The results in each case were practically identical; the differences being too slight to be detected in my apparatus. The spectrum exhibited, for instance, by 1 m.m. of the standard solution of didymium is found to be identical with the spectrum shown by the same solution diluted 20 times and viewed through a 20 m.m. cell.

It will be seen that in the case of 1 m.m., not only the line in the yellow at λ 582 ($1/\lambda^2$ 292)* is to be seen, but also two in the green at λ 525 ($1/\lambda^2$ 368) and λ 510 ($1/\lambda^2$ 382). Therefore, to get a more simple spectrum, I diluted the solution to 1 of didymium in 20 of liquid. I m.m. thickness of this shows little else than a broad faint trace of the line in the yellow, λ 582 ($1/\lambda^2$ 292).

(To be continued).

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.†

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

(Concluded from p. 17).

WHAT I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in al, of which only five are known at present.*

Among those possible for C_3H_6 there should be two isomers, propylene and trimethylene, and they are both already known. For C_3H_4 there should be three isomers: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 there should be two isomers, though neither of them are known as yet. Their composition and structure is easily deduced from ethane, ethylene, and acetylene, by methylation, methylenation, by acetylenation, and by carbonisation.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation, or from CHCH by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 = \begin{matrix} CHCH \\ CH_2 \end{matrix}$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because—

$$\begin{matrix} CH_2CH \\ CH \end{matrix} = \begin{matrix} CHCH \\ CH_2 \end{matrix}.$$

This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or isoallylene.

7. $C_3H_2 = \begin{matrix} CHCH \\ C \end{matrix}$ out of CH_3H_3 by symmetrical carbonisation, or out of CH_2CH_2 by acetylenation. This compound is unknown.

8. $C_3H_2 = \begin{matrix} CC \\ CH_2 \end{matrix}$ out of CH_3CH_3 by carbonisation, or out of CHCH by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylenation, and carbonisation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric bodies, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them, analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4, this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two and in carbonisation by four atoms, that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4, contains an even number of atoms of hydrogen, therefore all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbered parts.

The principle of substitutions explains with equal simplicity the conception of limiting compositions of hydrocarbons, C_nH_{2n+2}, which I derived, in 1861,† in an

* The λ and $1/\lambda^2$ lengths given here are only approximate.

† A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

* Conceding variable atomicity, the structurists must expect an incomparably larger number of isomers, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples HgCl and $HgCl_2$, CO and CO_2, PCl_3 and PCl_5.

† "Essai d'une théorie sur les limites des combinaisons organiques," par D. Mendeleeff, 2/11 aout 1861, *Bulletin de l'Académie s. d. Sc. de St. Petersbourg*, t. v.

empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; therefore, taking methane as a point of departure, if we imagine methylation effected $(n-1)$ times we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain—

$$CH_4+(n-1)CH_2, \text{ or } C_nH_{2n+2},$$

because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution—that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations, without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble ties which are so indispensable to structurists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamic principles of Newton, we can attain to that chief and fundamental object—the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides, and I count this for a circumstance of special importance, the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine, except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain, for chemistry, that unity of principle which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics, that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple, and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical, that is to say Newtonian, meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry, and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one, in a chemical compound—an atom of magnesium in the oxide of that metal, for example, for mercury, the atom of which is 8½ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind, the substitution of light for heavy atoms, need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, the properties of the substance.

This tendency to repetition, these periods, may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other: but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case, such, for example, as the earth and the moon, and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometricians have named epicycloidal, or the locus of a point in a circle rolling round another circle. But, in consequence of the influence of the moon, it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse, that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other, and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and suppose that, in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods changes have taken place, and are still going on, similar to those which pass rapidly before our eyes during the chemical reaction of molecules and the progress of molecular mechanics, may—we hope will—in course of time, permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolutions will only be possible, it seems to me, under the banner of Newtonian dynamics which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so

by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

ZIRCONIUM AND ITS ATOMIC WEIGHT.*

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

(Concluded from p. 18).

The Atomic Weight of Zirconium.

After what has been said it may appear that the previous determinations of atomic weight from the sulphate would be too high rather than too low, since there can be little doubt that Berzelius heated the salt above 400°. It does not follow, however, that by heating it for a short time at a moderately high temperature more than a small fraction of the salt would be brought under conditions favourable to decomposition, nor even would the temperature of the mass be such that the whole of the free sulphuric acid would be got rid of. And the fact that on repeating such a treatment no variation in weight occurred, would be no guarantee that the salt was normal zirconium sulphate. My own experiments show that to get rid of the excess of acid requires prolonged heating, and at the same time renewal of the atmosphere in the vessel containing the sulphate. Apropos of this, Berzelius's precaution to introduce into the crucible in the last stage of the ignition of the sulphate a little ammonium carbonate is a very necessary one, as it displaces often two or three m.grms. of sulphuric acid, which otherwise seems to remain in the crucible time after time and fix itself in the zirconia, when the crucible begins to cool. Furthermore, whatever previous experience may have been (for no special precaution is mentioned in any case), I have found it most difficult to ignite zirconium sulphate without loss ; the decomposition occurs with such violence at first, and the resulting zirconia is so extremely light, that, though every care was taken, varying results were got, even in igniting very gently over the Bunsen burner, some as low as 43 per cent of oxide instead of 43·3 at least. On carefully watching it was seen that minute particles of zirconia were being carried out of the crucible, although the cover fitted well. This loss was only avoided by enclosing the crucible within a second larger one, whose cover fitted quite closely and only communicated with the external atmosphere by a drawn-out neck, so that there were no air-currents. Even then, if the crucible was placed over the blowpipe flame at once, loss occurred, and it was necessary in every case to commence the operation over the flame of a Bunsen burner, and then after half an hour to transfer to the blowpipe.

Part of the determinations was made by Berzelius in the best way—that is, the zirconia was first precipitated by means of ammonia, and then the sulphuric acid determined in the filtrate by precipitation with barium chloride.

Having satisfied myself by careful comparative experiments that the results of both methods, under favourable conditions, correspond, I decided to adopt the dry method, viz., that of conversion of the sulphate into the oxide by ignition—

(*a*). Because it involved the least complicated operations and the fewest assumptions.

(*b*). Because under some circumstances basic zirconium sulphate is thrown down when ammonia is added to a solution of the sulphate.

In the following paragraphs are given the determinations of Berzelius and Mats Weibull from the sulphate, followed by those based upon my own experiments.

* A Paper read before the Royal Society, May 9, 1889.

Berzelius's Determination (*Pogg. Ann.*, vol. iv., p. 126).

From the analysis of the sulphate :—

SO_3	ZrO_2	:: 100	: 75·84
,,	,,	,,	: 75·92
,,	,,	,,	: 75·80
,,	,,	,,	: 75·74
,,	,,	,,	: 75·97
,,	,,	,,	: 75·85
Mean			75·853

ZrO_2	:	$2SO_3$	::	1·5171 : 2
Zr	:	O	::	5·591 : 1
Zr	:	H	::	89·23 : 1

Mats Weibull's Determinations.

$Zr(SO_4)_2$.	ZrO_2.	$\frac{ZrO_2}{Zr(SO_4)_2}$.
1·5499 grms.	0·6684 grm.	43·126 per cent
1·5445 ,,	0·6665 ,,	43·153 ,,
2·1683 ,,	0·9360 ,,	43·168 ,,
1·0840 ,,	0·4670 ,,	43·081 ,,
0·7913 ,,	0·3422 ,,	43·321 ,,
0·6251 ,,	0·2695 ,,	43·113 ,,
0·4704 ,,	0·2027 ,,	43·091 ,,
Total 8·2335 grms.	3·5523 grms.	43·146 per cent

Mean determination :—

Zr	: O	::	5·592 : 1
Zr	: H	::	89·255 : 1

My Own Determinations.

$Zr(SO_4)_2$.	ZrO_2.	$\frac{ZrO_2}{Zr(SO_4)_2}$
Portion A.		
2·62357 grms.	0·87785 grm.	43·381 per cent
2·6185 ,,	1·1354 ,,	43·360 ,,
Portion B.		
2·27709 grms.	0·08713 grm.	43·350 per cent
2·21645 ,,	0·96152 ,,	43·385 ,,
Portion C.		
1·75358 grms.	0·76107 grm.	43·4016 per cent
1·64065 ,,	0·7120 ,,	43·397 ,,
Portion D.		
2·33255 grms.	1·01143 grms.	43·361 per cent
1·81105 ,,	0·78485 ,,	43·337 ,,
Tot. 16·67344 grms.	7·23125 grms.	43·37 per cent

Maximum	Zr	: O ::	5·674 : 1
	Zr	: H ::	90·559 : 1
Minimum	Zr	: O ::	5·654 : 1
	Zr	: H ::	90·237 : 1
Mean	Zr	: O ::	5·664 : 1
	Zr	: H ::	20·401 : 1

Corrections in the Weighings.

The balance used could be read directly to $\frac{1}{10}$ m.grms., and had been proved to be a most reliable instrument. The weights were an excellent set by Standinger, of Giessen, and showed an average variation from the normal amounting to only 0·000035 grm.

Corrections were introduced—

(*a*). For the weights.

(*b*). For displacement of air, and variations in temperature and pressure.

(*c*). For variations arising by reason of the different hygroscopic conditions of the desiccator and balance case.

In any case where condensation of moisture was liable to occur this was corrected for by noting the increment of weight per minute for several minutes whilst exposed in the balance case, and then constructing a curve with increment of weight and time as ordinate and abscissa,

from which the necessary correction at the time of weighing could be introduced. In nearly all cases over two grms. of the sulphate was used for each determination, and even with two grms. a difference of one m.grm. in the weight of the zirconia obtained implies a difference of 0·25 in the atomic weight; it is, therefore, evident that in some previous determinations where less than a grm. has been taken, there is considerable risk of error in the atomic weight.

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

(Continued from p. 4).

The Ammonia Precipitate.

The filtrates and condensed washings from the silica having been united and set aside in a 200 c.c. flask, the greater portion of the liquid was poured into a beaker of the best hard Bohemian glass, concentrated, and ammonia was cautiously added to the hot liquid until the precipitate formed remained permanent on stirring. This precipitate was dissolved by adding the remainder of the acid liquid in the flask. The whole was then returned to the flask and sulphuretted hydrogen was passed in for fifteen to twenty minutes. The trace of sulphur precipitated was coloured from the presence of a trace of platinum, and sometimes lead. It was kept in closed flasks for two or three days, filtered through Gooch's, transferred to beaker, and concentrated. There was generally a slight cloudiness, which disappeared on further concentration; a few drops of nitric acid were added and the heating continued for some time. It was then precipitated carefully with ammonia in very slight excess, let stand for some time, and then filtered into the 200 c.c. flask, washed well with hot water, the washings concentrated in a platinum dish, and added to contents of flask, a little ammonia and ammonium sulphide added, and flask filled up to mark when cold. This portion serves for the estimation of lime and magnesia and last trace of silica.

The ammonia precipitate will contain much silica, ferric oxide, alumina if present, and also phosphoric acid in small quantity may be here, with possibly a trace of lime. It may be dealt with in a variety of ways.

First Method.—Dried on filter on sand-bath, transferred to crucible, ignited strongly, and weighed with the filter-ash, crushed with glass rod, fused with a little potassium bisulphate, boiled out with HCl and water, transferred to platinum capsule, evaporated to dryness, separated silica, and weighed in a small Gooch; added 1 grm. citric acid to filtrate, and then ammonia in very slight excess and acetic acid in slight excess. Tested with oxalate for lime. If none (or to filtrate if lime is present), added 30 c.c. magnesia mixture and ammonia, stirring well. If phosphoric acid precipitated it was filtered out and weighed. To the liquid or filtrate there was then added in a 100 c.c. stoppered flask ammonium sulphate to precipitate iron. After a day or two the iron sulphide is filtered, washed with water containing ammonium sulphide, dropped strong nitric acid upon filter, washed, evaporated to dryness on sand-bath, added a few drops nitric acid, and evaporated to dryness again two or three times. Ignited gently, dissolved in *aqua regia*, precipitated with ammonia in heat, filtered through small Gooch, ignited, and weighed as ferric oxide. The alumina is found by difference.

Second Method.—Ignited strongly and weighed. Transferred with ash of filter to a small steel mortar, crushed, ground fine in a small agate mortar, and fused in a platinum crucible with 5 or 6 grms. of the alkaline mixture, using a part to rinse the mortar. Conducted the fusion as usual, using 5 c.c. or more HCl to separate silica. The filtrate was nearly neutralised with ammonia and ammonium oxalate was added. Lime, if present, was filtered off. To the filtrate 1 grm. citric acid was added and ammonia in excess and 30 c.c. of magnesia mixture. The filtrate (or, if no phosphoric acid is present, the liquid) is treated as in method No. 1 to separate and determine iron. Alumina is found by difference.

Third Method.—In the absence of phosphoric acid in appreciable quantity the precipitate is dried on the sand-bath, but not ignited, and the total weight is not taken. The matter is crushed in a steel mortar, the filter is burnt, and the ash added to the precipitate and evaporated with HCl in a flat dish to separate silica. The concentrated filtrate is added to a solution of soda in a flat dish, heated, and the ferric oxide is separated through a small Gooch, and weighed. The filtrate is mixed in a small beaker with excess of HCl, and a little potassium chlorate is added, heated for some time, the alumina is precipitated with ammonia, collected in Gooch, washed, and weighed. The determination of the alumina in this method is direct. With most samples of glass, the quantities of lime being moderate, the trace carried down in the ammonia precipitate may be disregarded.

Fourth Method.—Dissolved the precipitate (after washing) with hot HCl, rather dilute, on the filter, washed the filter, and if it seemed that any silica had been separated out and retained by the filter, the latter is burnt and the ash added to the filtrate. This is then evaporated to dryness to separate silica, and its filtrate is treated as in method No. 3 to separate and determine iron and alumina directly. This method, like No. 3, is applicable only in the absence of appreciable quantities of phosphoric acid.

When precipitating with ammonia add the latter very cautiously to the hot liquid in very slight excess, and let stand a little before filtering. Avoid boiling, as it seems to render the precipitate less easily soluble in HCl.

In the absence of phosphoric acid, method No. 4 is better than No. 3. In presence of phosphoric acid method No. 2 is better than No. 1.

No. 3.— Three-quarter inch test-tubes going cloudy. Contains ferric oxide, 0·22 per cent; alumina, 1·11 per cent.

No. 10.—One inch test-tubes not cloudy. Ferric oxide, 0·3 per cent; alumina 2·01 per cent.

No. 29.—500 septem. flask, quite clear. Ferric oxide, 0·36 per cent; alumina, 2 per cent.

No. 34 A.—French glass tubing, not cloudy. Ferric oxide, 0·42 per cent; alumina, 2·29 per cent.

No. 34 B.—Ferric oxide, 0·14 per cent; alumina, 2·40 per cent. Neither of these determinations are trustworthy, the iron being too low and alumina too high.

No. 28.—A 300 c.c. cloudy flask. Ferric oxide, 0·29 per cent; phosphoric acid, 0·14 per cent. No alumina.

No. 22.—Cloudy pint tumbler. Ferric oxide, 0·3 per cent. No alumina.

No. 8.—Cloudy pipette. Ferric oxide, 0·27; alumina, 2·37.

A special test was applied to 5 grms. of the glasses in powder. It was mixed with 2 grms. ammonium fluoride in a flat dish, 3 c.c. pure sulphuric acid were added, and the dish was heated on the sand-bath and then over the lamp to expel most of the sulphuric acid. It was then boiled with dilute nitric acid, filtered, made up to 20 c.c., transferred to a small beaker, added 10 c.c. citric solution and ammonium nitrate and 10 c.c. molybdenum reagent, heated gently, and let stand. Most samples, if not all, contain a trace, at least, of phosphoric acid, as proved by this test. It is, however, in general, too small to interfere with the accuracy of the determinations if disregarded. It can only affect the determination of alumina in the second decimal. If more is present it must be separated.

No. 1.—Clear flask; reacts strongly. Ferric oxide, 0·21 per cent; alumina, 2·48 per cent.

No. 31.—Retort, quite clear, reacts slightly. Ferric oxide, 0·19 per cent; alumina, 0·82 per cent.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, July 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, six were recorded as "very slightly turbid." The remaining 162 samples were found to be clean, bright, and well filtered.

During the past month the progressive increase in degree of freedom from organic matter, manifested by the water supply during the first five months of the year successively, was not found to be sustained, but there was, on the contrary, a retrogression to about the degree recorded as prevailing a month or two back. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in 100,000 parts of the water, during each of the first six months of the year respectively, was found to be as set forth below,—the mean proportion of 0·144 grain of organic carbon observed during the month of May, corresponding as nearly as may be to about a quarter of a grain of organic matter per gallon:—

Parts of Organic Carbon in 100,000 *Parts of Water.*

January	0·170	April	0·154
February	0·161	May	0·144
March	0·161	June	0·157

A like appreciable, though not important, retrogression was observable in respect of the degree of colour-tint of the water, and of the amount of oxygen required to oxidise the organic matter present; and was noticeable alike in the supply furnished by all the Companies, whether taking their supply from the Thames or the Lea.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

On Free Fatty Acids in Oils.—Hugo Noerdlinger.—The author dissolves the oils in a mixture of ether and alcohol (previously neutralised), adds phenolphthalein, and titrates with decinormal potassa. The proportion of free acid in vegetable oils is considerably greater than it has been generally supposed, and fluctuates between very wide limits, being affected by the ripeness of the plants, by climate, exposure, and weather, &c.—*Zeitschrift f. Anal. Chemie*, Part 2.

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

SILVER is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in colour and lustre.

Whether metallic silver shall be reduced from its compounds in its normal or in an allotropic form, depends upon the reducing agent applied, so that it cannot be said with any certainty whether it exists in its compounds in its ordinary normal form or in an allotropic condition: the latter alternative seems at least equally probable.

These allotropic forms of silver are broadly distinguished from normal silver by colour, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerised form. Something analogous has already been observed with other metals, lead, and copper.

Much having been written, especially within the last few years, on the products of the reduction of silver compounds, a brief summary of what has appeared may be desirable before proceeding further. The study of this subject has led to remarkable divergencies of opinion on the part of the chemists engaged in it. Almost all the views advanced have been successively disproved by each subsequent publication. It follows that what has obtained a place in the text-books is almost wholly incorrect.

The earliest experimental work was Faraday's, but his product has been proved to be a mixture.† The next was the well-known paper of Wöhler, published in 1839. It is not my purpose here to enter upon a criticism of this memoir. If this illustrious chemist succeeded in obtaining by the means employed a true citrate of silver hemioxide,—as would appear from his analyses—no chemist since his time seems to have done so. The next publication to Wöhler's was that of Von Bibra, who used Wöhler's method and, whilst affirming that he obtained a similar citrate, found an entirely different constitution for the corresponding chloride; for, instead of obtaining a hemichloride Ag_2Cl, he gives, as the result of fifteen concordant analyses, the constitution of his product as Ag_4Cl_3.‡ A citrate, to yield such a chloride (if such a chloride exists) by the simple action of hydrochloric acid, could scarcely have the constitution assigned to it by both Wöhler and V. Bibra.

In 1882 Pillitz published two papers.§ He commences by disputing the probability of the existence of Ag_4O on grounds of valency; namely, as implying that oxygen may be quadrivalent. Although it is very doubtful that any one has up to the present time obtained Ag_4O, the argument seems futile, as are many arguments deduced from supposed laws of valency. Similar reasoning would make Ag_2Cl impossible, which substance undoubtedly exists, and it would also deny the existence of K_2Cl, which stands upon such authority as that of Rose, Kirchhoff, and Bunsen.‖ Pillitz carefully examined the so-called hemioxide precipitated by alkaline solutions of

* *American Chemical Journal*, Vol. xxxvii., No. 222.

† G. H. Bailey and G. J. Foster, *Chem. Soc.*, 1887, 416. *Berichte D. Ch. G.*, xx., Ref. 360.

‡ Erdmann, *J. Prakt. Chim.*, 1875, 120, 39. Von Bibra precedes his paper with a brief summary of the conclusions reached by previous chemists on the subject of the action of light and chemical reducing agents on silver compounds. The collection is interesting, as showing to what inconsistent and even contrary opinions careful observers have come on these reactions.

§ *Zeitschrift fur Ann. Chemie*, xxi., p. 27, p. 496.

‖ "Gmelin Kraut," ii., 1, 72.

antimony and tin, and could find no trace of Ag_4O in any of them. He did not examine Wöhler's products.

The first person to deny categorically the existence of Wöhler's series of hemi-compounds of silver appears to have been Dr. Spencer Newbury. In two interesting papers* he describes a repetition of Wöhler's methods, and declares it to be impossible to obtain products of constant composition. The red solution taken by Wöhler to be argentous citrate, Dr. Newbury concludes to be a suspension of finely divided† silver. Muthmann, after a careful examination of Rautenberg's products, concludes that that chemist was wholly in error in asserting the formation of compounds of chromic, molybdic, and tungstic acids with silver hemioxide. He next studies the red liquid obtained by Wöhler's process, and comes to the same conclusion as Newbury: that it consists of finely divided silver suspended in water.

I shall not dispute the correctness of this opinion in the case of the liquid examined by these two chemists. At the same time I cannot accept the tests of solution employed by Muthmann. That a substance will not pass through a dialyser shows that it is colloidal, and is no proof whatever that it is not in solution. Animal charcoal takes up many substances from true solutions. Decolourisation by animal charcoal is no proof whatever that the colour removed was not in true solution. By freezing, the molecular condition of a substance may be changed. Muthmann found that when the red liquid was mixed with gum-water and precipitated by alcohol, the precipitated gum carried down with it the red substance, thence deducing that it was only in suspension. This conclusion is scarcely justified. A solution of litmus was mixed with gum-water and precipitated with alcohol; the mass of the litmus went down with the gum, a trace only appeared in the filtrate. With Hoffmann's violet, the same result. Yet no one, I think, will assert that these two substances do not make true solutions in water. Even, however, if these arguments could be admitted they would not apply to the solutions presently to be described, which can be proved by optical means to be true solutions. I propose presently to show that silver may exist in a perfectly soluble form, dissolving easily and abundantly in water. Starting from this it may show all degrees of solubility down to absolute insolubility, still, however, existing in an allotropic form, and quite distinct from normal or ordinary silver. The solutions formed are as perfect as those of any other soluble substance.

Wöhler's process was next repeated by G. H. Bailey and G. J. Foster, who came to the conclusion that no citrate of hemioxide was formed, and that Wöhler's results must be rejected.

Von der Pfordten‡ endeavoured to obtain hemi-compounds of silver by acting on the nitrate with an alkaline solution of sodium tartrate, and also with phosphorous acid. His determinations were made volumetrically, based on an opinion that a permanganate solution acidified with sulphuric acid would dissolve silver hemioxide, but not metallic silver. Previously to receiving his paper I had found that sulphuric acid, even diluted with ten times its bulk of water, was capable of acting on finely divided normal silver, and of dissolving an easily recognised quantity. V. d. Pfordten's conclusions were thus vitiated entirely. It should, however, be remarked that the difficulties of the subject are extremely great. In his last paper§ this chemist abandons his views as to the existence of silver hemioxide; so that at the present time the formation of Ag_4O by Wöhler's method, or by any other known method, is admitted by no one. That such an oxide may exist appears by no means improbable. The existence of Ag_2Cl and K_2Cl seems almost to involve that of Ag_4O and K_4O. This latter product Davy believed that he had obtained. The black substance which V. d. Pfordten formerly regarded as Ag_4O he now takes to be silver hydrate, Ag_4H_2O.

The reduction products described by V. d. Pfordten are strongly distinguished from those which I shall presently describe by two decisive reactions:—

1. None of his products could be amalgamated with mercury (l. c., 2296). All of mine readily amalgamate.

2. None of my products give off the slightest trace of gas when treated with dilute sulphuric acid. All of his do so (l. c., 2291).

Moreover, the difference of appearance is extremely great.

Early in the year 1886 I took up the study of the reduction products of silver in connection with that of the photo-salts. I commenced with Wöhler's process, giving it up after a few trials as affording no satisfactory results, and sought for a more reliable means. This I found in March, 1886, in a reaction which I still use: namely, the reduction of silver citrate by ferrous citrate. At first, however, the results obtained were most enigmatical, the products very unstable, and impossible to purify. Much time was lost, and the matter was given up more than once as impracticable. Eventually, by great modifications in the proportions, stable products and capable of a fair amount of purification were got. Even the earlier and less pure forms were exceedingly beautiful; the purer are hardly surpassed by any known chemical products.

The forms of allotropic silver which I have obtained may be classified as follows:—

a. Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

b. Insoluble, derived from *a*, dark reddish brown while moist; when dry, somewhat resembling *a*.

c. Gold silver, dark bronze whilst wet; when dry, exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-coloured. Insoluble in water, appears to have no corresponding soluble form.

Properties Possessed by all the Varieties in Common, and Distinguishing them all from Normal Silver.

All these forms have several remarkable properties in common.

1. *That of Drying with their Particles in Optical Contact, and consequently Forming a Continuous Film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a lustre as high as that of metallic leaf. C, when so treated, would be taken for gold leaf. But this property is much better seen by brushing the pasty substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is as good. A and B form bluish green mirrors, C gold or copper-coloured mirrors.

2. *The Halogen Reaction.*—When any of these allotropic forms of silver are brushed over paper, and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colourations are obtained. The experiment succeeds best with substances that easily give up the halogen, such as sodium hypochlorite, ferric chloride, iodine dissolved in potassium iodide, &c. But indications are also obtained with alkaline salts, such as ammonium chloride, &c., though more slowly and less brilliantly. With sodium hypochlorite the colours are often magnificent intense shades with metallic reflections, reminding one of the colours of a peacock's tail. Blue is the predominating tint. These are interference colours, caused by thin films, but whether of a normal silver haloid or a hemi-salt cannot be said. When silver leaf (normal silver) is fastened to paper and a comparative trial is made, the contrast is very striking. This matter will be more particularly examined in the second part of

* *Am. Chem. Journ.*, vi., 407; viii., 196.
† *Berichte der D. Ch. Ges.*, xx., 983.
‡ *Ibid.*, xx., 1455.
§ *Ibid.*, xx., 2288.

this paper, and is mentioned here as one of the reactions distinguishing allotropic from ordinary silver.

3. *The Action of Acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal grey silver; even acetic acid, not too much diluted, does this. It is important to remark that this change takes place absolutely without the separation of gas. I have more than once watched the whole operation with a lens, and have never seen the minutest bubble escape.

4. *Physical Condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces, and by moderate trituration yield a fine powder.

(To be continued).

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts, Manufactures, and Medicine, &c.; with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By A. H. Allen, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Vol. iii., Part I.—Acid Derivatives of Phenols, Aromatic Acids, Tannins, Dyes, and Colouring Matters. London: J. and A. Churchill.

Mr. Allen's great work is very far from declining in value and interest as it approaches completion, and is characterised both by general accuracy and by completeness.

In speaking of zinc phenol sulphonate the author notices a curious instance of blundering in high places. The British Pharmacopœia, after directing this salt to be prepared by "heating a mixture of carbolic acid and sulphuric acid, saturating with zinc oxide, evaporating, and crystallising," remarks that the solution of the product is "only rendered faintly turbid by chloride of barium."

We notice a curiously named mixture, "dextro-saccharine," which is simply commercial glucose got up with a small proportion of Fahlberg's saccharine. The product is said to be indistinguishable in taste from the best cane sugar. If this is correct as regards human taste, bees would very soon detect the imposture.

Among the varieties of tannin, tabulated on p. 79, we notice an animal tannin present in the corn-weevil. A similar compound, according to the *Transactions and Proceedings of the Entomological Society* for 1887 (xxxiii.), has been found in a variety of beetles which feed on vegetable matter. The author very clearly points out the improbability—not to say the impossibility—of devising any method for the accurate determination of tannins in all kinds of tanniferous matters.

In the section on writing-inks we find no mention of the useful method of comparing specimens of writing by different lights (sun-light, gas, monochromatic flames, &c.) if it is desired to ascertain the identity or diversity of the inks used.

The bulk of the book is taken up with a very elaborate account of dyes and colouring matters. After general remarks on the constitution of colouring matters, their relation to textile fibres, to mordants, and on their colouration, these compounds are described under the following heads:—The nitro- and nitroso-groups, the aurine class, the phthaleines, the azo-dyes, the rosanilines, the safranine group, the anthracene colours, and the sulphuretted and unclassified coal-tar dyes. In this last class figures a compound bearing the name curcumene, which is objectionable on the same principle as are tropæoline and, in former days, roseine, azaleine, &c., names now obsolete or obsolescent because deceptive.

The colouring-matters of natural origin are very fairly described. The author justly remarks that the methods for extracting and producing such colours would have been greatly improved of late years had not the attention of tinctorial chemists been monopolised by the coal-tar colours. We are, indeed, convinced that, at least as far as indigo is concerned, there is good prospect for improvements of this kind. The ammonia process and the selection of ferment-cultures both are exceedingly promising. A foot-note states that, by the addition of ammonia to the leaves during fermentation, the yield of colour may be increased 100 per cent.

Concerning woad it must be remarked that it is used not so much for the trace of indigotine which it contains as for the favourable influence which it exerts on the fermentation in the warm vat.

Attention is called to the important fact that when indigo is reduced to indigo-white in the vat, and re-oxidised to indigo-blue on exposure to the air, a certain proportion is never recovered. The author suggests this loss as an interesting and possibly remunerative subject for investigation.

We regret that Mr. Allen retains the name indigo-carmine for extract of indigo. We submit that the name "carmine" should be strictly confined to the well-known preparation of cochineal, and not extended to coloured pastes in general.

We notice with satisfaction that the so-called "close" red woods, santal-wood, barwood, camwood, and calliatura, are clearly distinguished from the soft or open red woods, such as brazil-wood, peach-wood, sapan, &c. In some works, written by supposed practical men, we have known these classes to be confounded.

The author next gives in three successive chapters instructions for the recognition of colouring matters for the examination of commercial dyes and for that of dyed fibres. These chapters will be found exceedingly valuable.

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—No one who has any acquaintance with the liquid which Dr. Emerson Reynolds has named "Thiocamf" will question its value as a disinfectant. This liquid is not a novelty. In 1846, Parkes patented the preparation "obtained by passing sulphurous acid gas over finely granulated camphor until the camphor becomes liquid (by the absorption of sulphurous acid gas)." It was proposed to use this as a solvent of india-rubber, gutta percha, resins, &c. (see Specification, No. 11,147, A.D. 1846).

Indiarubber, when acted on by this liquid, is altered in precisely the same way as when acted on by dry sulphurous acid gas. There is no difficulty in preserving the liquid in a closed bottle, but if a piece of sheet indiarubber be wetted with it, the sulphurous acid is absorbed, leaving an efflorescence of camphor. Its effect on certain vegetable oils is curious and interesting.—I am, &c.,

Thomas T. P. Bruce Warren.

Tamworth Villa, Earlham Grove,
Forest Gate, E.

Examination of Manna.—A. Kresnel (*Pharm. Post* and *Chem. Zeitung*) dissolves one part of manna in one part of water, adds ten times the volume of alcohol at 95 per cent, heats to a boil, and filters through wool previously freed from fat. After the evaporation of the alcohol there remains pure mannite, which should form 75 per cent of a good manna.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 1, July 1, 1889.

On Barium Malonates.—M. Massol.—The author describes three neutral salts, the tetrahydrate, dihydrate, and the anhydrous compound. The dihydrate is of great stability, and if heated for some hours to 140° it retains the same composition.

The Acetates and Benzoates of the Active and the Racemic Camphols. Preparation of a Pure Dextro-Borneol Identical with the Borneol of Dryobalanops.—A. Haller.—This memoir does not admit of useful abstraction.

Zeitschrift fur Analytische Chemie. Vol. xxviii., Part 2.

Analytical Studies on Phosphododekamolybdic Acid: the Conditions of its Formation, and its Separation as an Ammonium Salt.—Dr. F. Hundeshagen.—The substance of this very extensive memoir will be given at some length.

Determination of Tungsten in Richly Tungstiferous Alloys.—Dr. Jos. Preusser.—From 0·5 to 1 grm. of the alloy, broken up in a steel mortar, finely pulverised, and sifted through lawn, is heated in a shallow porcelain capsule on a Bunsen burner, before the blast, or in the muffle, until the colour, which is at first greenish yellow, passes into a completely pure yellow. Over the Bunsen burner, this is generally effected in a few hours. No loss of tungstic acid is occasioned by excessive or prolonged ignition. The mass is then rinsed into a porcelain capsule and evaporated down once with aqua regia. It is then repeatedly evaporated to dryness with hydrochloric acid, and heated on the air bath to 120°. It is then taken up in dilute acid, let stand for some hours, and filtered. The tungstic and silicic acids left on the filter are ignited in a platinum crucible, after incineration of the paper, intimately mixed with 3—4 parts of sodium carbonate, and ignited before the blast for thirty minutes. When cold the melt is dissolved in hot water, filtered, and any tungstic acid not opened up is again fused with sodium carbonate. The filtrate, containing the tungstic acid as a sodium salt, is mixed with hydrochloric acid, when the tungstic acid separates out almost entirely as a white hydrate, but for its complete separation, the filtrate, after the addition of acid, must be evaporated down to dryness. It is then dissolved in water, and, after standing for a few hours, it is filtered by means of the filter-pump, and washed with a dilute solution of ammonium nitrate. The precipitate along with the paper is placed in an Erlenmeyer flask. Any hydrate adhering to the porcelain capsule is dissolved off by means of ammonia, and added to the contents of the flask, which are brought into solution as ammonium tungstate by the addition of ammonia and gentle heating on a hot plate. The silicic acid remains practically undissolved. The slight error due to the sparing solubility of silica in ammonia may be disregarded. The solution is freed by filtration from the silica evaporated down in a tared porcelain capsule, and the residue ignited until its weight is constant. If tin is present in the alloy the method of Donath and Müller is applicable. The metal is roasted, evaporated to dryness with aqua regia, heated to 120°, taken up in dilute acid, and the residue is treated according to the instructions of the authors abovementioned, with the addition of the method just described for separating tungstic acid from silica.

The Analysis of Butter.—L. F. Nilson.—The substance of the author's process will be inserted as soon as practicable.

A Modification of the Kjeldahl Process.—Prof. J. W. Gunning.—Already inserted.

Examination of Commercial Peptones.—J. Kõnig and W. Kisch.—This memoir does not admit of useful abstraction.

On Polaristrobometric Chemical Analysis.—H. Landolt.—A treatise which first appeared in the *Transactions of the Royal Prussian Academy of Sciences* (1887, vol. xlviii.), and which is here given verbally. It does not admit of abridgment.

The Use of Potassium Manganate in Analysis.—Ad. Jolles.—(*Repertorium der Anal. Chemie*).

Separation and Determination of Zinc.—J. Riban.—From *Bulletin Soc. Chimique de Paris.*

Separation and Determination of Boric Acid.—H. N. Morse and W. M. Burton.—From the *American Chemical Journal.*

Determination of Boric Acid.—S. L. Penfield and E. S. Perry.—From the *American Journal of Science.*

The Coloured Reactions of the Compounds of Carbon.—E. Nickel.—(An Inaugural Dissertation). Some of the reactions here mentioned will be inserted hereafter.

The Compositron of Wine Vinegars Obtained by Fermentation.—H. Eckenroth (*Pharm. Zeitung*).—The specific gravity of wine vinegars ranges between 1·0116 and 1·0149. If it falls below 1·0100 the presence of alcohol may be suspected, which is of rare occurrence. The extractive matter is between 0·35 and 0·51 per cent. Glycerin generally exists only in traces from 0·05 to 0·1 per cent. No constant relation between the proportions of glycerine and of acetic acid can be traced. The acetic acid is from 4 to 7 per cent, and in good samples does not fall below 6 per cent. Tartar is a main characteristic of a pure wine-vinegar, but for its determination 1 litre should be evaporated. The total ash rarely exceeds 0·25 per cent, and in most cases is not above 0·15.

Detection of Cochineal in Articles of Food.—Lagorge.—From the *Journal de Pharmacie et de Chimie.*

Examination of Balsam of Peru.—C. Donner (*Pharm. Central Halle*).—The author gives methods for detecting sophistications with benzoine and storax.

The Identification of Lanoline.—G. Vulpius (*Archiv. d. Pharmacie*) proposes the following reaction:—If a few centigrms. of lanoline are dissolved in chloroform, and if this solution is cautiously stratified above an equal volume of undiluted sulphuric acid in a test-tube, there appears at the contact of both liquids a fiery brown red ring. The chloroform above the ring has a violet reflection.

Determination of the Value of Ipecacuanha.—A. Lyons.—From the *American Journal of Pharmacy.*

Comparative Determination of Belladonna Leaves.—Coblentz.—From the *Pharmaceutical Journal.*

Valuation of Preparations of Strychnia, and Separation of Strychnine from Brucine.—O. Schweissinger (*Archiv der Pharmacie*).—No particulars are given.

Titration of Bitter Almond Water.—W. Kübel (*Arch. der Pharmacie*).—The author uses, instead of magnesium hydroxide, basic magnesium acetate.

Detection of Carbonic Acid in Potassa Lye.—A. Koster (*Archiv der Pharmacie*).—In a mixture of 10 c.c. saturated solution of gypsum and 5 c.c. distilled water potassa lye free from carbonate occasions no turbidity, whilst if one-fifth per cent of carbonate is present turbidity appears.

The Application of Nitroso-β-naphthol in Quantitive Analysis.—G. von Knorre.—Following out the methods which the author, in conjunction with Ilinski, has elaborated for separating cobalt and nickel, and also iron and aluminium, he has examined the behaviour of this reagent with other metals. It was found that in an acetic solution, besides cobalt and iron, copper is thrown down quantitatively by means of nitroso-β-naphthal, whilst aluminium, lead, cadmium, calcium, magnesium, manganese, nickel, mercury, and zinc remain in solution. The details of the various separations will be given hereafter.

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THE CHEMICAL NEWS.

Vol. LX. No. 1548.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

(Continued from p. 30).

In the year 1886 (*Proc. Roy. Soc.*, xl., 502, June 9, 1886; Chem. News, liv., 27, July 19, 1886) I demonstrated from experiments on the fractionation of didymium that this element was very probably a compound capable of being resolved into a number of constituents, each represented by a single band, like the cases of yttrium and samarium, which give bands by phosphorescence. In Krüss and Nilson's case, the batch of crude earth contained in any single mineral was examined as a whole without any attempt to separate the earths, and the composition of some of these minerals is extraordinarily complex, euxenite for example containing, after removal of the other metals, the rare bodies Ce, La, Di, Sm, Yt, Er, Tr, Ho, Tm, Th, De, Sc, Dy, Be, Nb. Ta.

In my own case the didymium earths, upon which I formed the "one band one element" theory (Chem. News, liv., 27) were in a much more simple state, as the whole of the yttrium group, including erbium, holmium, thulium, &c., and others, had been removed, and the earth under examination probably contained little besides didymium and lanthanum, with traces only of samarium, yttrium, and calcium. But not even here was the earth under examination in a state of even approximate purity.

There are at least two points in these researches that I must touch, since they illustrate the necessity of great caution in drawing conclusions from an examination of absorption-spectra. Paul Kiesewetter and Krüss (*Ber.*, xxi., 2310; Chem. News, lviii., 75, 91) have recently published a paper on this subject, although it goes no further, nor indeed so far as the previous communication of Krüss and Nilson. They have examined gadolinite, and find that some constituents of didymium and samarium are absent, notably those which produce the group of lines in the green to which I have already referred. In my own laboratory I have worked for the last two years almost exclusively upon the earths from gadolinite—of which I have obtained a large quantity from Fahlun—and there is not the shadow of a doubt that in my gadolinite earths the lines reported absent by Kiesewetter and Krüss are present in abundance.

Some hitherto unexplained condition doubtless rendered these lines invisible to Kiesewetter and Krüss; perhaps the presence of some other earths, or some condition of concentration or acidity. In the light of this knowledge I do not see how we can take the results of Krüss and Nilson or my own as final.

Concerning the influence of one body upon another little is yet known, but that little is of sufficient importance to make us very careful how we interpret absorption-spectra when uncorroborated by chemical results. Lecoq de Boisbaudran and Smith have pointed out some important modifications produced in absorption-spectra by an excess of acid (*Compt. Rend.*, lxxviii., 1167), and later on Soret (*Compt. Rend.*, September 15, 1879) verified these observations. Brauner and others have recorded experiments on mixing solutions of didymium and samarium; they find, in the case of a didymium solution showing the group of three bands, λ 476, 469, 428 ($1/\lambda^2$ 430·4, 441·3, 454·6), that by adding a dilute solution of samarium, all three of these bands vanish without any appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come in their place (Brauner, *Trans. Chem. Soc.*, 1883, xliii., 286). In my own experiments, I find that from a solution of erbia which originally shows no trace of the strong didymium band lying between λ 596 and 572 ($1/\lambda^2$ 281 and 305), appreciable quantities of didymium can certainly be squeezed out by fractionation.

Owing to its complicated nature, Kiesewetter and Krüss consider gadolinite an unfavourable source of didymium for these investigations, and recommend that a large quantity of earth from keilhauite should be systematically worked up, for the reason that keilhauite didymium is more simple in constitution.

The Erbium Group.

It is known that a certain oxide, ten years ago called erbia, and regarded as belonging to a simple elementary body, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Clève, Brauner, and others into at least six distinct earths—three of them, scandia, ytterbia, and terbia, giving no absorption-spectra, whilst others, erbia (new), holmia, and thulia, give absorption-spectra.

In Fig. 8A I have represented the old erbium absorption-spectrum, as it was known down to the year 1878. In Fig. 8B, as in the case of didymium, I have given for diagrammatic purposes certain lines which, not seen in unfractionated erbia, belong to bodies capable of being separated from it by fractionation.

The first to announce that erbium was not a simple body was Delafontaine, who in 1878 (*Compt. Rend.*, lxxxvii., 559; Chem. News, xxxviii., 202) published an account of philippium, a yellow oxide characterised by a strong band in the violet, λ 400 to 405 ($1/\lambda^2$ 625, to 623), a broad, black absorption-band in the indigo-blue, λ about 450 ($1/\lambda^2$ 494), two rather fine bands in the green, and one in the red.

The history of philippium is curious, and I may perhaps be allowed to give it in some detail. A year after Delafontaine's discovery Soret (*Compt. Rend.*, lxxxix., 521; Chem. News, xl., 147) published a paper in which he declared that philippia was identical with his earth X. The next month, in a note on erbia, Clève (*Compt. Rend.*, lxxxix., 708; Chem. News, xl., 224) said he could not identify Soret's X with Delafontaine's philippia, as the latter was characterised by an absorption-band in the blue which occupied the same place as one of the erbia bands. In February, 1880 (*Compt. Rend.*, xc., 221; Chem. News, xli., 72), Delafontaine returned to the subject, enumerating 10 new earths in gadolinite and samarskite, viz., mosandra, philippia, ytterbia, decipia, scandia, holmia, thulia, samaria, and two others unnamed. He said that the properties of philippia were those of Soret's X and Clève's holmia, and proposed that the name "holmia," being a duplicate name for an already known earth, should be discarded in favour of philippia. In July, 1880 (*Compt. Rend.*, xci., 328; Chem. News, xlii., 185), Clève repeated his former statement that philippia was not the same body as Soret's X or holmia. Delafontaine next withdrew all he had said about the absorption-spectrum of philippium, and decided that it had no absorption-spectrum (*Archives de Genève*, [3], 999, 15). Finally, Roscoe (*Chem. Soc. Journ.*, xii., 277), in an elaborate chemical examination of the earth-metals in samarskite, proved that philippia was a mixture of yttria and terbia. From a prolonged chemical study of these earths I have since come to a similar conclusion; but a spectroscopic examination of the earth left on igniting some specially purified crystals of "philippium formate" tested in the radiant matter tube, has shown

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

me that in the separation of Delafontaine's philippium the yttria undergoes a partial fractionation, and three of its components or meta-elements, Gζ, Gδ, and Gβ, are present in great abundance, while others, Gα and Gη, are almost if not quite absent.

Shortly after the announcement of philippium, Soret (*Compt. Rend.*, lxxxvi.. 1062) described an earth which he provisionally called X. This was soon found to be identical with an earth subsequently discovered by Clève (*Compt. Rend.*, lxxxix., 479; Chem. News, xl., 125), and called by him holmia. Soret admitted the identity, and agreed to adopt Clève's name of holmia. Fig. 9 shows the absorption-spectrum of X or holmia. It consists of a very strong band in the extreme red, λ 804 ($1/\lambda^2$ 155), two characteristic bands in the orange and green, λ 640 and 536 ($1/\lambda^2$ 244 and 347), besides fainter lines in the more refrangible part of the spectrum, and a number of bands in the ultra-violet.

Simultaneously with the discovery of holmia, Clève announced the existence of a second earth from erbia, which he called thulia. Fig. 10 shows the absorption-spectrum of thulia. It consists of a very strong band in the red, λ 680 to 707 ($1/\lambda^2$ 216 to 200), and one in the blue, λ 464·5 ($1/\lambda^2$ 462). The residual erbia, after separation of these earths, gives a simpler absorption-spectrum, shown in Fig. 11.

In 1886 (*Compt. Rend.*, cii., 1003, 1005) Lecoq de Boisbaudran showed by fractional precipitation of Soret's X and by spectroscopic examination of the simple fractions, that this X, or holmium, consisted of at least two elements, one of which he named dysprosium, retaining the name of holmium for the residue left after deducting dysprosium. Fig. 11 shows the absorption-spectrum of dysprosium; it has four bands, λ 451·5, 475, 756·5, 427·5 ($1/\lambda^2$ 490·5, 443, 175, 547). The new holmium gives an absorption-spectrum shown in Fig. 13.

As regards dysprosium, I pointed out (*Proc. Soy. Soc.*, xl., 502), at the time it was first announced, that I had obtained a solution in which one of the bands claimed for dysprosium, the one at λ 451·5 ($1/\lambda^2$ 490·5), was very strong, while the others were absent. As M. de Boisbaudran associates the bands at λ 475 ($1/\lambda^2$ 443) and λ 451·5 ($1/\lambda^2$ 490·5) as both belonging to dysprosium, and as I have obtained an earth which gives λ 451·5 ($1/\lambda^2$ 490·5) strong with no trace of λ 475 ($1/\lambda^2$443), it is evident that the conclusion I arrived at in 1886—that dysprosium itself consisted of at least two simpler bodies—is correct.

The old spectrum of erbium (Fig. 8) shows two faint bands at λ 550 and λ 493 ($1/\lambda^2$ 331 and 409); the second being broader than the first. These bands do not occur in the spectra of holmium, thulium, dysprosium, or the new erbium. In a long-continued fractionation of the erbia group of earths, carried out with an ample supply of the old erbia, I find an earth giving these two bands concentrating at one end, and the bands become stronger. At the same time two other new bands are making their appearance. This, therefore, points to the existence of still another earth belonging to the erbium group.

Incandescence Spectra.

Another distinct method of spectrum analysis depends on the examination of the spectrum of the light emitted by a solid substance when raised to incandescence. Almost the only known example of this is obtained in the case of erbia (*ibid*, xl., 77, January 21, 1886). It is scarcely known that if erbia in the solid state is illuminated by the electric or other bright light, and examined in the spectroscope, it gives a spectrum of black lines and bands as distinct as the Frauenhofer lines. The spectrum of bright lines emitted when solid erbia is heated to incandescence in the blowpipe flame has been more often observed; in this case the lines come out luminous on a faintly continuous background, whilst the reflection spectrum just mentioned is composed of black lines sharply defined and much more luminous, upon a continuous spectrum. Holmia and thulia, components of old erbia, possess a similar property (Chem. News, lvi., 165).

Phosphorescence Spectra.

I will now deal with phosphorescence spectra. Not a few chemists and physicists, conspicuous among whom is Ed. Becquerel, have carefully studied the phenomena of phosphorescence. Phosphorescence may be excited by elevation of temperature, by mechanical action, by electricity, and by exposure to the rays of the sun, and the light thus given off—for example, in the case of fluor-spar, has been examined by means of the spectroscope. In my own spectroscopic research I have dealt with the phosphorescence occasioned by the impact of the molecules of radiant matter upon certain phosphorescent bodies, or what I have ventured to call molecular bombardment.

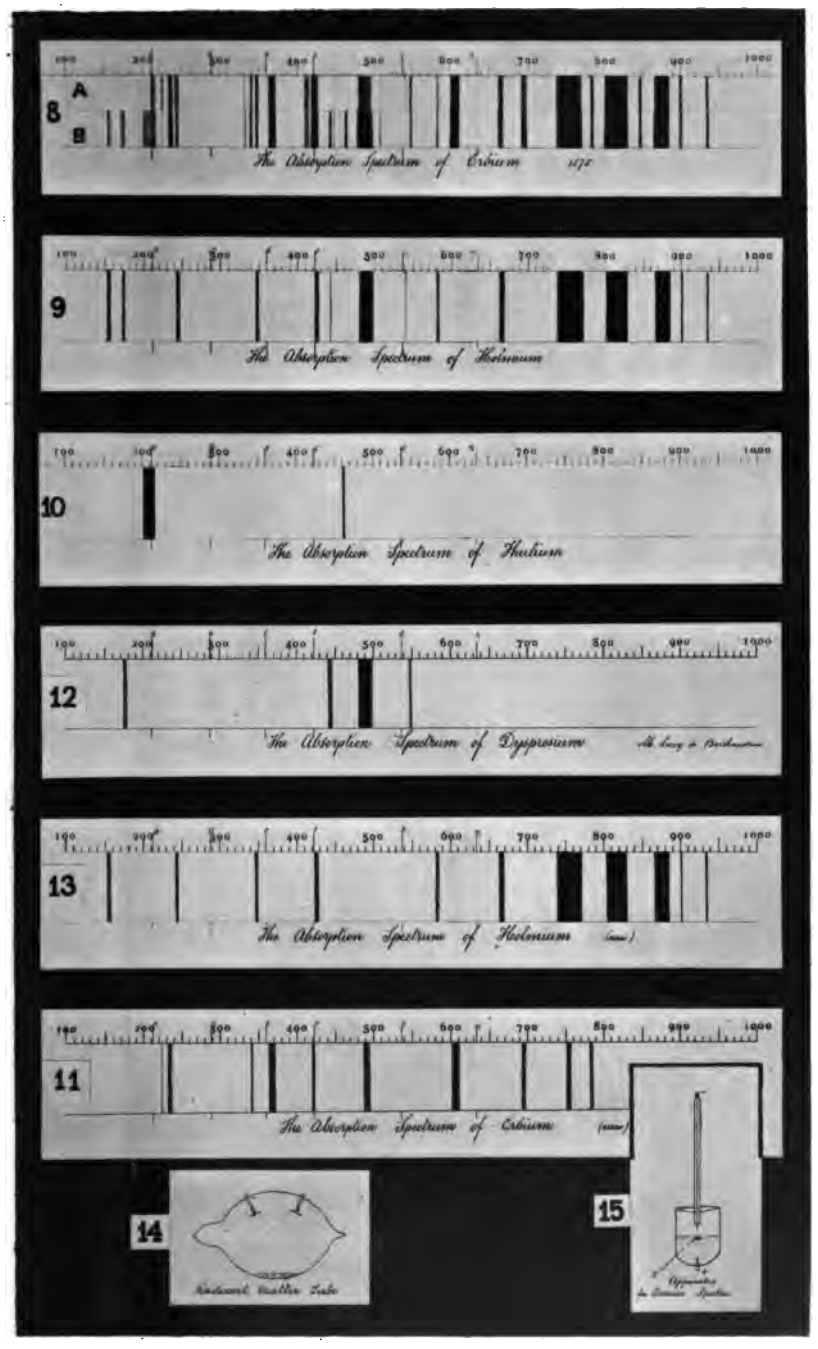
It is not necessary for me to describe the mode of procedure further than to say that the substance under examination is placed in a very high vacuum—a vacuum which varies in degree in the case of certain earths. Fig. 14 shows the form of radiant matter tube I prefer. In such a vacuum, when submitted to the action of the induction current, substances phosphoresce very differently from what they do when treated similarly at the ordinary pressure of the atmosphere. Under such circumstances the spectroscopic examination of matter affords what I have called the radiant matter test. The number of substances which are thus phosphorescent is very considerable. Glass of different kinds, according to its composition, phosphoresces with various colours. Phenakite (glucinium silicate) phosphoresces blue; spodumene (aluminium and lithium silicate) gives off a rich golden-yellow light, whilst the emerald phosphoresces crimson, and the diamond, being exceptionally sensitive and brilliant, throws off a bright, greenish white light.

The ruby, one of the minerals I examined earliest in this manner, glows with a rich, brilliant, red tone, quite independent, as regards its depth and intensity, of the colour of the stone as seen by daylight; the pale, almost colourless specimens, and the highly prized variety of the true "pigeon's blood," all phosphoresce with substantially the same colour.

There are several varieties of phosphorescence spectra, or rather, substances to be submitted to the radiant matter may be previously prepared in divers manner, so as to give modified results. Thus—

a. An earth alone—of course in the solid state—may be very strongly ignited, and, when cold, examined in the radiant matter tube. This method differs from the use of the spectrum of incandescent solids above noticed, solely in the final test of molecular bombardment. Of this variety of phosphorescence spectra, we may take, as examples, the phenomena yielded by alumina, yttria, didymia, and lanthana.

b. Another modification applicable in the treatment of the less pure earths takes as material the sulphates of the earths. The substance under examination is first treated with strong sulphuric acid; the excess of the acid is then removed by heat, and, lastly, the sulphate is heated to a point just short of driving off all the sulphuric acid. It is then placed in the radiant matter tube, and when the exhaustion has been carried as far as necessary, the induction current is passed through (*Phil. Trans.*, Part III., May, 1883). This method gives a spectrum of broad bands, easily recognised, but by no means easy to measure. The spectroscope used should have a low dispersive power, and should not have a very narrow slit. In the case of yttrium sulphate the bands are more analogous to the absorption-bands seen in solutions of didymium than to the lines given by spark spectra. If examined with a high magnifying power the outlines of the bands become less definite. The bands are seen much more sharply when the current first passes than after it has been passing for some time and the earth has become hot. On cooling, the bands again appear sharply defined.



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.

This method of observing the constitution of the rare earths, duly aided by delicate and prolonged chemical processes, has permitted us to push our investigations further than had previously seemed practicable. It enables us to determine whether we have reached the end of our investigations—a consummation which had hitherto been vainly sought. It has enabled us to prove that yttrium, samarium, &c., are not simple, homogeneous bodies. But what of the constituents into which they have been thus resolved? Suppose we refine them down until each displays merely one spectral band—what then? Is each one of such bodies barely differentiated from its neighbours chemically or physically, entitled to rank as an element? If so, as I pointed out in the Address which I had the honour to deliver before you in March last, we shall have to deal with further perplexing questions, arising in part from the relation of such elements to the periodic system. In a discussion of the elements, not as yet published, Dr. Wundt maintains that their possible number cannot exceed 79. But I myself see no definite and sufficient reason for limitation to this number. If these bodies are not elementary, possessing as they do the properties commonly regarded as characteristic of an element, we must be prepared to show why not?

Whatever rank may ultimately be assigned to these substances, they must, for convenience sake, have names as soon as our knowledge of their properties is in a sufficiently advanced state to allow of their removal from the suspense account.

(To be continued).

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

(Concluded from p. 33).

The Lime and Magnesia.

THE solution containing ammonium sulphide (in order to precipitate the manganese) was made up to 200 c.c. and filtered. 100 c.c., equal to 1 grm. of glass, was taken to estimate the lime and magnesia. HCl was added in slight excess and the liquid was concentrated and filtered; ammonia in excess was then added and ammonium oxalate. The mixture was set aside for several hours, filtered, generally through a small Gooch, and the filtrate was tested for magnesia by adding powdered microcosmic salt in large excess and stirring well. If more than traces of magnesia are present the calcium oxalate is dissolved in HCl, re-precipitated, filtered, and the filtrate is added to the liquid in which the bulk of the magnesia was precipitated. The calcium oxalate is ignited, gently at first, and is then reduced to lime by the blast. The magnesia is obtained as pyrophosphate by strong ignition over the spirit-lamp.

Of the 200 c.c. solution 50 c.c. were filtered, acidulated with HCl, concentrated, filtered, mixed with 10 c.c. ferric chloride solution of known strength, precipitated with ammonia in heat to recover last trace of silica. If the lime was first removed by oxalate the excess of the latter in the filtrate renders the ferric oxide very difficult to wash, and a trace of silica may possibly be carried down with the lime. When the lime was removed in one experiment the iron precipitate weighed only 0·001 less than when the lime was left in. In glass containing moderate quantities of lime the author has therefore not removed this before recovering the silica. The last fraction of the 200 c.c. solution, including the washings of the filter, was kept in case of accident.

No. 28.—Lime, 4·92 per cent; magnesia, 0·27 per cent.

No. 34 A.—Lime, 6·04 per cent. Magnesia, trace only, not determined.

No. 34 B.—Lime, 6·06 per cent. Magnesia, trace only.

No. 3.—Lime, 8·76 per cent. Magnesia, trace only.

No. 1.—Lime, 4·02 per cent; on repeating operation, 3·96 per cent. Magnesia, imponderable.

No. 5.—Lime, 5·62; magnesia, 0·21.

No. 31.—Lime, 8·16. Magnesia, trace.

No. 29.—Lime, 5·96. Magnesia, trace.

No. 22.—Lime, 6·32. Magnesia, trace.

No. 10.—Lime, 9·96. Magnesia, trace.

No. 8.—Lime, 7·22. Magnesia, trace.

The following table shows the complete analysis of some of the specimens:—

No. 3.	
K_2O	2·27
Na_2O	15·75
Lime	8·76
Ferric oxide	0·22
Alumina	1·11
Silica	70·61
	98·72
No. 10.	
K_2O	2·08
Na_2O	15·68
Lime	9·96
Ferric oxide	0·30
Alumina	2·01
Silica	68·94
	98·97
No. 28.	
K_2O	10·08
Na_2O	10·70
Lime	4·94
Ferric oxide	0·29
Phosphoric acid	0·14
Silica	73·13
Magnesia	0·27
	99·55
No. 22.	
K_2O	0·30
Na_2O	19·40
Lime	6·32
Ferric oxide	0·30
Silica	73·06
	99·38
No. 34 A.	
K_2O	4·02
Na_2O	16·84
Lime	6·04
Ferric oxide	0·42
Alumina	2·29
Silica	69·86
	99·47
No. 29.	
K_2O	5·44
Na_2O	13·62
Lime	5·96
Ferric oxide	0·36
Alumina	2·00
Silica	71·49
	98·87
No. 8.	
K_2O	1·80
Na_2O	19·18
Lime	7·22
Fe_2O_3	0·27
Al_2O_3	2·37
Silica	67·23
	98·07

No. 31.

K_2O	0·66
Na_2O	15·22
Lime	8·16
Fe_2O_3	0·19
Al_2O_3	0·83
Silica	73·70
	98·75

No. 1.

K_2O	4·68
Na_2O	14·38
Lime	4·02
Ferric oxide..	0·21
Alumina	2·48
Silica	72·49
	98·26

CHEMISTRY UNDER HIGH PRESSURE.

By H. N. WARREN, Research Analyst.

Of all the forces that the chemist is able to bring to bear upon or aid in his investigations, perhaps none is more important or stands less rivalled than that of force in its simplest form, namely pressure; and with respect to this agent no form is apparently more indicated to aid in scientific research than that evolved automatically, or more correctly speaking by encouraging a portion of the substance under examination, contained in a suitable enclosure, to considerably expand, through subjecting the same to a more or less elevated temperature, and by so doing either retard or prevent further dissociation of the remaining portion in consequence of the pressure thus exerted. This particular form of operation, as is well known, is frequently adopted for the decomposition of farinaceous substances, when desirous of converting the starch present into that of glucose, previous to estimating the same.

The mode of construction of these tubes and the manipulation of the same have already been described (Chemical News, vol. lviii., 155). Since that period, however, a somewhat more robust apparatus has been made use of, and intended for dry heats. The plan of construction being almost essentially the same as in the former instance, save that the copper casement is replaced by that of wrought iron, to the extent of four inches thick, being provided with a drilled orifice of half an inch circumference, and extending to within an inch of the bottom, inside of which is inserted a small platinum or porcelain tube, according as the nature of the experiment may command. The platinum tube with its contents being hermetically sealed before the oxyhydrogen blowpipe, and after inserting the same packed with dry magnesia, the top being afterwards closed by the aid of a powerful screw extending within the orifice to the length of two inches, and terminating in a handle, so as to ensure of sufficient leverage power being applied to readily expose the contents after cooling.

In order to test the efficiency of the apparatus the inner or platinum tube was half filled with pure precipitated calcium carbonate, closed, and heated to whiteness by the aid of a wind-furnace. On opening the same, after cooling, a stick of perfectly fused substance was obtained, possessing all the properties of marble, being somewhat more translucent. By substituting for the platinum a porcelain tube, at the same time using a somewhat lower temperature, arsenicum metal was readily fused, and presented considerable lustre. Among various other experiments may be mentioned the decomposition of potassium silicon fluoride when in admixture with zinc, from which the silicon was afterwards separated in the form of fine needle crystals. A modified form of apparatus is at present under construction in which both the temperature and pressure may be lowered at will. Several interesting results have been already obtained, and it is hoped to ultimately lead to some improvements in organic synthesis.

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ON THE

STABILITY OF THE FATTY GLYCERIDES.

By THOMAS T. P. BRUCE WARREN.

I omit from the present consideration animal oils and fats generally, and include all the vegetable fixed oils which I have had an opportunity of working on, which are fluid at 15·5° C.

It is customary to divide oils into two classes, viz., drying and non-drying oils. Anyone who has given attention to this subject must feel that this division is wanting in scientific precision. So long as it is a question relating to oils suitable for making paints this division may be technically useful, but if we go further into the matter of lubricants we must confess that there is an absence of that demarcation between the two classes of oils, as implied strictly by this division.

The drying or clogging properties of an oil depend mainly on its stability. An oil will not dry or clog until it is decomposed, and in proportion to the rapidity of this change so is the drying quality of an oil increased. The general explanation is that the glycerin is oxidised into carbonic acid and the fatty acids into a thickened mass or dry product.

Cotton and rape-seed oils decidedly thicken when heated air or oxygen is passed into them, especially if the oils themselves are heated to 300° C. Oils of poppy-seed and walnuts will thicken readily on exposure to warm air; olive oil does not thicken under the same circumstances.

When an oil is oxidised, its iodine absorption is diminished, whilst its electrical resistance is increased. The product obtained with sulphur chloride is very dark, in some cases almost black.

Although I have passed ozonised oxygen into pure olive oil for days under exposure to strong sunlight, I have not been able to obtain a product with sulphur chloride darker in colour than that obtained from the original oil. I therefore conclude that pure olive oil has a very remarkable stability when compared with other oils.

Oils which have parted with a portion of their glycerin will yield a product containing a larger portion of matter soluble in carbon disulphide than the same oil when fresh. Cotton-seed oil, deprived of its glycerin is readily soluble after treatment with sulphur chloride.

The effects of heat on oils show that olive oil is more stable than sesame oil.

The non-suitability of an oil as a lubricant may be ascertained by the diminished iodine absorption when oxygen is passed into it. An oil which "gums" or clogs on a bearing will be found to have its iodine absorption diminished in proportion to its tendency to clog. The value of this as a test for a machine oil or lubricant is of very great importance, especially if a proper mechanical arrangement is not available for testing.

The thickening of an oil on a bearing depends on its stability. We have, on a rapidly revolving spindle, every facility at its bearings for oxidation. In an extreme case the oil becomes quite sticky when the journals have cooled down. As friction involves extra work to be done, it is obvious that an oil which reduces this to a minimum must be one which, besides reducing friction, does not involve internal work on itself. Many adulterations may be recognised by carefully observing the effects of friction on a journal provided with a thermometer.

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

(Continued from p. 36).

A. *Soluble Allotropic Silver.*

A SOLUTION OI ferrous citrate added to one of a silver salt produces instantly a deep red liquid. (Ferrous tartrate gives the same reaction, but is less advantageous). These red solutions may either exhibit tolerable permanency or may decolourise, letting fall a black precipitate. It is not necessary to prepare the ferrous salt in an isolated form, a mixture of ferrous sulphate and sodic citrate answers perfectly.

When, however, concentrated solutions are used with a large excess of ferrous sulphate, and a still larger one of alkaline citrate, the liquid turns almost completely black. It should be stirred very thoroughly for several minutes to make sure that the whole of the precipitated silver citrate is acted upon by the iron. After standing for ten or fifteen minutes the liquid may be decanted, and will leave a large quantity of a heavy precipitate of a fine lilac-blue colour. It is best to adhere closely to certain proportions. Of a 10 per cent solution of silver nitrate, 200 c.c. may be placed in a precipitating jar. In another vessel are mixed 200 c.c. of a 30 per cent solution of pure ferrous sulphate, and 280 c.c. of a 40 per cent solution of sodic citrate. (The same quantity of ferrous sulphate or of sodic citrate in a larger quantity of water will occasion much loss of the silver product). I think some advantage is gained by neutralising the ferrous solution, which has a strong acid reaction, with solution of sodium hydroxide: as much may be added as will not cause a permanent precipitate. To the quantities already given, about 50 c.c. of 10 per cent soda solution. The reaction takes place equally well without the soda, but I think the product is a little more stable with it. The mixed solution is to be added at once to the silver solution.

The beautiful lilac shade of the precipitate is rather ephemeral. It remains for some time if the precipitate is left under the mother-water, but when thrown upon a filter it is scarcely uncovered before the lilac shade disappears and the precipitate takes a deep blue colour without losing its solubility. It may be washed either on a filter or by decantation with any saline solution in which it is insoluble and which does not affect it too much. On the whole, ammonic nitrate does best, but sodic nitrate, citrate, or sulphate may be used, or the corresponding ammonia salts. Although in pure water the precipitate instantly dissolves with an intense blood-red colour, the presence of five or ten per cent of any of these salts renders it perfectly insoluble. I have usually proceeded by adding to the precipitate (after decanting the mother-water as completely as may be, and removing as much more as possible with a pipette) a moderate amount of water; for the above quantities about 150 c.c. Much less would dissolve the precipitate but for the salts present: this much will dissolve the greater part, but not the whole, which is not necessary. A little of a saturated solution of ammonic nitrate is to be added, just enough to effect complete precipitation.

As the material appears continually to change, the amount of washing needed must depend upon the object in view. If wanted for analysis, the washing must be repeated many times until ferric salt ceases to come away, but no amount of washing will entirely eliminate it. After seven or eight solutions in pure water and as many precipitations, the material is to be thrown on a filter, the liquid forced out as completely as possible with a pump, and then the ammonic nitrate washed out with 95 per cent alcohol until the filtrate leaves nothing on evaporation. The substance at this point is still soluble in water, though much less so than at first. During the washing the solubility slowly but steadily diminishes, a fact rendered noticeable by less and less ammonic nitrate being needed to precipitate it from its solution.

Analysis.—The product after thorough washing, as above described, with alcohol, was dried at ordinary temperatures or a little above, and was then reduced to very fine powder and washed again with water as long as anything dissolved. It was then dried at 100° C. in water-bath. Three silver determinations were made—

A1	.. .. ..	97·31 per cent silver
A2	.. .. ..	97·18 ,, ,,
B	.. .. ..	97·21 ,, ,,

A1 and A2 were made with different portions of the same material, B with different material prepared in exactly the same way.

The substance therefore contained on an average 97·27 per cent of silver. The nature of the residue would decide whether the material was silver with a certain amount of impurity firmly attached to it, or whether we had to do with silver in chemical combination with other elements.

The filtrate from the silver chloride in analysis A2 was evaporated to dryness, and was found to contain chiefly iron and citric acid. The iron was thrown down as sulphide, re-dissolved in nitric acid, precipitated hot, washed with boiling water, and gave 0·8947. The residue therefore consisted of ferric oxide and citric acid, probably in the form of ferric citrate, and attached so strongly that even the very careful and prolonged washing given failed to remove them. Stronger means would be required than could be used without altering the condition of the substance. The conclusion, therefore, seemed to be justified that the material consisted of uncombined silver simply mixed with impurity.

To verify this conclusion by additional evidence, the substance was examined as to its behaviour when heated. For if any other element were chemically combined with the silver it would only be (in view of the high percentage of silver) hydrogen or oxygen. We might have to do with a hydride, analogous to Wurtz's hydride of copper, or possibly an oxide, but not probably as Ag_4O would contain only 96·43 per cent of silver.

The presence of either hydrogen or oxygen in combination with silver seems to be pretty certainly negatived by the action of dilute sulphuric acid on this (and the two other substances, B and C, to be described farther on). They are all converted into grey metallic silver without the slightest escape of gas. This seems tolerably conclusive in itself, and the result of exposing a great number of specimens of all the forms A, B, and C to the action of heat, was equally so. As the object was to expose the fresh and moist material to a gradually increasing heat from that of boiling water to a low red heat without interrupting the process, the following arrangement was found convenient:—

A piece of Bohemian glass tube about six inches long was sealed in the lamp at one end, the other closed with a rubber cork, through which passed a small gas delivery tube, and another tube passing into a small test-tube partly filled with water and having another tube through the cork passing under the surface of the water, thus preventing regurgitation. The material was thus first exposed for some hours to a heat of about 150° C. in a chloride of calcium bath; this was next removed, and the heat continued to low redness. Only traces of gas were evolved, and this was found to be in all of the many trials made, carbonic acid, derived from the citric acid adhering. This treatment was repeated many times with all the different varieties of the substance, and with the same result. The temperature was always raised sufficiently high to ensure the complete conversion of the material into normal grey silver, but in no case was oxygen or hydrogen set free.

It could not be overlooked that in all these trials the material had passed into an insoluble form before the silver determination was made. There remained, there-

* *American Chemical Journal*, Vol. xxxvii., No. 222.

fore, this possibility: that the silver, so long as soluble, might be in combination with citric acid, and that its change to the insoluble condition was caused by its separating from the citric acid. It seemed desirable that this view should be tested. As the object was to determine the condition of the silver in the substance as originally formed, avoiding as far as possible to change that form by attempts at purification, the only course available was to determine the ratio between the silver on the one hand and the citric acid on the other, either excluding from the determination, or else removing, that portion of the citric acid which was combined with sodium (sodic citrate being used in excess) or with iron. The first attempt was to exclude without removing it, by using Wolcott Gibbs's ingenious method of precipitating the base by hydrogen sulphide, and determining the acid thus set free in a solution originally neutral. It was ascertained by careful experiment on weighed quantities of pure anhydrous citric acid, that exact titration could be made with the aid of phenolphthalein. The silver was next re-dissolved and estimated as chloride. A large number of determinations were made, but the method proved unsatisfactory. It was found that portions of the same material operated upon separately gave different (even widely different) results. In fact, this very discordance was in itself a proof than to stœchiometrical combination existed between the silver and the citric acid.

The importance of the matter led me to take it up again with different means, estimating the citric acid by Creuse's method. In this method the solution, after being reduced to a small bulk, is exactly neutralised (with ammonia or acetic acid), is treated with a slight excess of barium acetate, and then mixed with twice its bulk of 95 per cent alcohol, let stand a day, and filtered and washed with 65 per cent alcohol. In igniting, a few drops of sulphuric acid convert the barium salt into sulphate, in which form the estimation is made. A preliminary trial with a weighed quantity of citric acid showed that this method gave fairly good results. I was obliged to vary the method somewhat: the precipitate of barium citrate carried down with it enough iron to render it ochrey in appearance. It was, therefore, after thorough washing with 65 per cent alcohol till every trace of barium acetate was removed, dissolved on the filter with dilute hydrochloric acid (acid 1, water 10), in which barium citrate is extremely soluble and washed through. This was followed by still weaker acid, and finally with water. From the filtrate, sulphuric acid precipitated snow-white barium sulphate.

But this method requires that both the sulphates and the excess of sodic and ferric citrate shall first have been perfectly removed. The blue precipitate was therefore washed with dilute solution of ammonic nitrate until this was effected. The necessity for this purification was regrettable as introducing a possibility of a change during the treatment. It was, however, indispensable that the ferrous, ferric, and sodic citrates present should be got rid of. The material after this treatment was still freely soluble in water, to a dark red solution. An examination of its absorption spectrum showed it to be still a true solution. From this solution the silver was first removed by H_2S, and then the citric acid was determined in the above described way. (If the silver were thrown down by hydrochloric acid, the reliability of the citric determination would be impaired). Next, the silver sulphide was converted into chloride and weighed. The result gave the ratio—

1 grm. silver to 0·03195 grm. citric acid.

In this case washing out the sulphates, &c., was an affair of several days. The work was repeated, reducing the time as much as possible. The material was precipitated, decanted as soon as settled, thrown upon a filter-pump, and the funnel kept constantly full of ammonic nitrate in dilute solution by a wash-bottle. By using very thick paper and a powerful pressure the entire washing was rapidly finished, so that in about six hours from first precipitation the material was thoroughly washed, re-dissolved, and again filtered and placed under the action of H_2S. The result was—

1 grm. silver to 0·0130 citric acid.

When these relations are reduced from weights to equivalents they become—

No. 1. 1 equiv. citric acid to 55·63 equivs. silver,
No. 2. 1 „ „ „ 193·7 „ „

indicating both that the proportion of citric acid present is variable, and that it is certainly not in stoichiometrical combination with the silver in the substance examined.

It has been already said that these solutions, before being acted upon by H_2S, were examined optically and found to be true solutions. The inference, therefore seems to be very strong that there exists an allotropic form of silver freely soluble in water. This is a property so exceptional in a metal that I have admitted it with much hesitation. The principal arguments are as follows:—

The content of silver in the various products was very carefully and, I believe I may say, quite accurately determined; it was extremely high, always above 97 per cent. As already remarked, this virtually excludes the presence of all elements except hydrogen, and possibly oxygen. These elements were carefully searched for, but their presence could not be detected. To suppose that we had to do with a mixture in which some compound of silver was mixed with metallic silver was not possible, for as the whole was soluble we should still have to admit the solubility of silver.

We have consequently to deal with a substance containing over 97 per cent of silver, and neither hydrogen nor oxygen in combination with it, the remaining 2 or 3 per cent fully accounted for by ferric oxide, and citric acid determined as present as accidental impurity; the substance itself readily amalgamating with mercury by simple friction, nevertheless abundantly soluble in water. If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself.

Whether in solution it exists as a hydrate, that is, in more intimate combination with one or more equivalents of water, cannot be said with entire certainty; but the easy amalgamation with mercury seems hardly to favour that view. No means could be found for settling the question absolutely. Certainly at 100° C. all water is expelled, but this is, of course, not an argument. All the water is not expelled by indefinite exposure to a vacuum over sulphuric acid. But the proportion left is very small.

The material examined was in all cases as nearly as possible the same as that originally precipitated, but absolute identity could not be obtained. The purification absolutely necessary effects some change. This is shown by the colour. The freshly precipitated material dissolves to a blood-red liquid, by great dilution yellowish red. The purified substance gives a darker red solution, which with dilution remains still red. Of the nature of the substances in the condition in which they were analysed, I can speak with some positiveness, and these include a substance soluble in water and, nevertheless, appearing to be nearly pure silver.

The constitution of the lilac-blue substance at the moment of formation, and whilst still under its mother-water, is a matter of more difficulty; it could not be said with certainty that it was not in some way altered in the purification. Much time and labour were spent in endeavouring to settle this point, without entirely satisfactory results, and I am at present engaged in the search for a better method.

When this blue soluble substance, purified either by washing very moderately by ammonium nitrate or by washing with pure water, using those portions which remain undissolved after most has been carried through the

filter, is brushed over paper and dries rapidly, it exhibits a very beautiful succession of colours. At the moment of applying, it appears blood-red; when half dry, it has a splendid blue colour with a lustrous reflection; when quite dry, this metallic effect disappears, and the colour is mat-blue. Examined with a polariser, it shows the same characters as to two reflected beams of light polarised in planes perpendicular to each other that are described further on under B.

When the blue substance prepared in either way dries more slowly in lumps, the result is very variable; sometimes it is bright bluish metallic; sometimes dull red colour, with a metallic reflection only where it has dried against a smooth surface.

(To be continued).

DERIVATIVES OBTAINED FROM MONOCHLORDINITROPHENOL AND BASES OF THE AROMATIC SERIES.*

By EDGAR F. SMITH.

It is well known that picric acid combines readily with bases and the higher hydrocarbons of the aromatic series to form well-crystallised and stable compounds. It has, however, not been observed that phenols containing less than three nitro-groups together with other negative groups or elements, possessed this acidic property of picric acid. Several years ago (*Am. Chem. Journal*, i., 180) I discovered that when monochlordinitrophenol (1 : 2 : 4 : 6) and aniline were brought together there resulted a rather stable derivative, which did not decompose in aqueous solution until after prolonged boiling. Recently I have obtained derivatives with this same chlordinitrophenol and the bases and hydrocarbon mentioned below.

The phenol itself forms yellow-coloured needles, melting at 80° C. Its *α-naphthylamine* derivative consists of brownish yellow crystalline tufts, composed of velvety needles, melting at 131° C. and solidifying at 110° C. It was obtained by dissolving equal quantities of the phenol and α-naphthylamine in hot alcohol; on cooling, the new compound separated quite rapidly. It dissolves in warm water. The *o-toluidine* derivative, obtained by heating together equivalent quantities of the phenol and toluidine, consists of golden yellow plates, soluble in hot alcohol. It melts at 140° C. and solidifies at 115° C.

The *p-toluidine* compound separated from its alcoholic solution in reddish-yellow needles, quite soluble in water, and melting at 157° C. With *urea* the phenol does combine, but the union is evidently unstable, since by exposure to the air a gradual change in colour was perceptible. The *carbazol* compound consists of intensely red-coloured needles, melting at 121° C. It dissolves quite readily in alcohol. With *p-nitraniline* long needles were obtained. Their colour resembled that of chromic acid. It was rather difficult to obtain them pure. The *anthracene* derivative forms plates with an intense red colour. The union is not stable, and exposure to the air causes a gradual decomposition. The *morphine* compound is made up of bundles of needles, having a deep vermilion colour. It dissolves in alcohol, and melts at 97° C. The combination with *propylamine* is a yellow crystalline solid; that with *strychnine* consists of yellow nodular crystals, melting at 212° C.

The determination of the carbon and hydrogen in the aniline compound, and that of the nitrogen in the α-naphthylamine and *o*-toluidine derivatives, show that all the products described above are very probably combinations of a molecule of the chlordinitrophenol, with a like amount of the basic body.

I have further observed that dichlormononitrophenol, obtained in the nitration of dichlorsalicylic acid (*Am. Chem. Journal*, viii., 98), does not unite with aniline, so that it would seem that the acidic character of the phenol reached its limit with the dinitro-product; and that union with bases such as those given above, is not possible when but one NO_2 group is present.

The facts here communicated are to be regarded as preliminary to an investigation now going on, but which must shortly be suspended for some months.

* Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Messrs. James Hall, B.A., B.Sc., and J. W. Slater were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas William Dukes, Cape Town, South Africa; Theodore Francis Garrett, 36, Drakefell Road, St. Catherine's Park, Hatcham, S.E.; Eric Henry Jackson, B.Sc., Harefield, Morley Road, Southport: William Whitehouse, Myrtle Villa, Dixon's Green, Dudley.

The following were elected Fellows of the Society:—Edward Wightman Bell; William D. Cargill, B.Sc.; George William Howard; Frederick Charles Knight; Henry W. Morrow, B.S.; D. O'Mahoney; Benjamin Phillips; Robert Redwood; Emanuel Roberts; Robert M. W. Swan.

The following papers were read:—

62. "*Observations on the Melting-point of some Salicylic and Anisic Compounds.*" By W. H. Perkin, Ph.D., F.R.S.

The author, after referring to his paper published in the Journal of the Society in 1867, in which methylated and ethylated salicyl aldehyds are described as nearly colourless fluids which do not solidify when cooled in a freezing mixture, and to the apparently contradictory results of Voswinckel (*Ber.*, 1882, 2024)—who states that methylated salicyl aldehyd is a solid melting at 35°—points out the curious fact that, although this latter aldehyd does not easily crystallise in a freezing mixture, it can be made to do so; the crystals, however, melt at about 2·7—3°. On evaporating an ethereal solution of the aldehyd, he obtained prismatic crystals, having the melting-point given by Voswinckel, and it was found that if the oily aldehyd be touched with one of these it immediately becomes a solid mass having a melting-point of 35°. On re-melting this solid, and then cooling in a freezing mixture, crystals melting at 2·7—3° can again be obtained. It is therefore established that methylated salicyl aldehyd forms crystals of two kinds, having melting-points differing by about 32°.

Ethylated salicyl aldehyd can also be made to crystallise; the crystals melt at about 6° or 7°.

Anisic aldehyd also crystallises when cooled; although a para-compound, it melts at a lower temperature than either modification of methyl salicyl aldehyd, viz., at 0·02°.

Ethylic anisate easily crystallises (m. p. = 7°), but ethylic methyl-salicylate has not as yet been obtained in a crystalline condition.

63. "*The Action of Propionyl and Butyryl Chloride on Phenol.*" By W. H. Perkin, Ph.D., F.R.S.

In preparing phenyl propionate and butyrate by means of phenol and propionyl and butyryl chloride, the author has observed that secondary products are also formed,

which are proved to be new phenols containing acid radicles in place of hydrogen in the phenyl-group, viz., $C_3H_5O{\cdot}C_6H_4{\cdot}OH$, and $C_4H_7O{\cdot}C_6H_4{\cdot}OH$. They are both crystalline compounds, propionylphenol melting at 148·5°, butyrylphenol at 91°; they are soluble in ammonia solution.

Phenylic acetate, which has been previously described as an oil, was obtained in a crystallised condition; it melts at 20° and boils at 211° (corr.).

Phenylic butyrate, which has not been previously prepared, is an oil boiling at 227—228° (corr.).

64. "*The Nature of Solutions as Elucidated by a Study of their Freezing Temperatures.*" By S. U. PICKERING.

A series of determinations of the freezing temperatures of mixtures of sulphuric acid and water was undertaken in order to obtain further confirmation of the existence in solution of the various hydrates which had been indicated by the densities, heat of dissolution, heat capacity, and electric conductivity of these solutions, as well as to throw some light on Raoult's method of determining molecular weights.

The determinations with solutions containing over 4 per cent H_2SO_4 were attended with considerable difficulty, as the solution does not freeze, but one of its constituents crystallises out, the change being identical in nature with the crystallisation of a salt from a saturated solution; what has to be determined, therefore, is the temperature at which the given solution becomes saturated. This was done by cooling the liquid down until a good crop of crystals was obtained; it was then put in a vessel of water, and the rise of temperature noted at every half minute; the temperature at which the last crystals had disappeared was signalised by a sudden alteration in the rate of this rise.

The author has, so far, plotted the results only against percentage composition. The general results are represented by three independent curves, in which water, $H_2SO_4{\cdot}H_2O$, and H_2SO_4 itself are the substances which crystallise out.

The first of these curves is represented by an approximately straight line as far as 8 or 9 per cent H_2SO_4, falling at the rate of about 0·5° for every 1 per cent; it then curves rapidly downwards, the crystallising temperature of a 30 per cent solution being 36°; a little beyond this point it appears to become almost vertical. From 30 to 77 per cent no freezing-points have been attained. At this latter strength the crystallisation of the monohydrate begins. This crystallisation is represented by a curve with two branches, having its highest point at 84·5 per cent (the composition of $H_2SO_4{\cdot}H_2O$) and 8·5°, and falling away from this point on either side, at first gradually, and then abruptly. At about 94 per cent this curve meets that representing the crystallisation of H_2SO_4, the temperature being −31°; the H_2SO_4 curve rises from this point in an approximately straight line up to 100 per cent and 10·35°, when it turns abruptly down again in a curvilinear direction, the determinations having been extended as far as 101 per cent.

A closer inspection of these several curves shows that none of them are continuous, but that they are made up of separate curves or straight lines, which seem to be quite independent of each other, and show breaks of a most marked character, often corresponding to differences five or ten times greater than the experimental error. These breaks occur in every case at the same points as those observed by the author in the densities and other properties, and are of a very much more certain character than in any of the other cases. Of the 17 hydrates of sulphuric acid which he previously indicated, 12 are very satisfactorily confirmed by the present observations; the other five (H_2SO_4 with 2, 4, 5, 9, and 13 H_2O) would be shown only in that portion of the diagram where no freezing-points have yet been reached. In addition to this, there appear to be three other breaks, which the previous work would have been insufficient to show, at 98·7, 86, and 82·5 per cent, corresponding to—

$$12H_2SO_4{\cdot}H_2O,$$

$7(H_2SO_4{\cdot}H_2O){\cdot}H_2SO_4$, and $7(H_2SO_4{\cdot}H_2O){\cdot}H_2O$, as well as a break at 100·7 per cent, representing $27H_2SO_4{\cdot}SO_3$, and at 100 per cent, or H_2SO_4 itself. It is especially noteworthy that the breaks at the extreme end of the curve corresponding to H_2SO_4 with 500, 1400, and 5000 H_2O have been fully confirmed.

The marked character of these breaks (which are apparent without any differentiation) leads to the hope that the method may be applicable in the case of solutions of organic liquids where other methods would fail.

Each of the three main curves which represent the general results tend downwards at an increasing rate as we pass from the highest points in them, and this tendency would also be exhibited if the results were plotted against molecular instead of percentage composition. This, the author shows, is what their character should be if hydrates were formed in solution, whereas on the physical theory of solution, they should tend downwards at a diminishing rate; so that the general form of the curves, independent of there being breaks in them, is conclusive in favour of the hydrate theory.

Passing on to the bearing of these results on Raoult's method, the author repeats his assertion that, at the best, this method could only give us the molecular weights of substances in the gaseous condition at the temperature of the determination, for in dilute solutions the molecules of the dissolved substance are as far removed from each other as they are when vaporised.

There are, however, no theoretical considerations which justify our regarding the molecular weight thus obtained in the same light as that obtained from vapour-densities. The vapour-density is a constant within experimental error throughout a very long range of conditions, whereas the lowering of the freezing-point could only be a constant on the supposition that dissolution is entirely physical and that the dissolved molecules act independently of the solvent. The present results show that it is not a constant, and that we have no grounds for supposing it to be such even with extremely dilute solutions. The irregularities and breaks which characterise the whole results have been traced back as far as a 0·1 per cent solution, and a further extension of the determinations, if possible, would simply reveal a continuation of these irregularities. On the other hand, it must be admitted, as, indeed, the practical results prove, that these irregularities would often lead to no great error in the molecular weight found, provided the solutions used are not too strong.

The author shows that such would be the case with the sulphuric acid curves, when the crystallisation of water is used to determine the molecular weight of H_2SO_4, or that of sulphuric acid to determine the molecular weight of H_2O. But the case is otherwise when we use the crystallisation of the monohydrate to determine the molecular weight of H_2SO_4 on the one hand, and H_2O on the other. Within 5 per cent of $H_2SO_4{\cdot}H_2O$ we should get results such as 18 for H_2SO_4 and 6 for H_2O. This shows that, although Raoult's method may give approximately correct results in many cases, we can never rely on it without performing an extensive series of experiments. There are no theoretical considerations which would lead us to suppose that it is reliable, and this investigation proves that each case has peculiarities of its own, which may lead to an entirely erroneous molecular weight.

65. "*Note on the Determination of the Molecular Weight of Substances in Solution, especially Colloids.*" By HENRY E. ARMSTRONG.

The fundamental conception underlying the now very general acceptation of the Raoult methods of determining molecular weight is undoubtedly the conception introduced by Van't Hoff that substances are present in dilute solutions in a state comparable with the gaseous state (cf. Ramsay, *Chem. Soc. Proc.*, 1889, p. 44). But in gases, even in the most imperfect, the individual molecules exercise a very slight mutual attractive influence; otherwise, in fact, the gaseous state could not subsist. When

liquefaction ensues, it would appear to be owing to, and to involve the exertion of, such mutual intermolecular attractions; and however continuous the states of gas and liquid may appear from a mathematical standpoint, the continuity would seem to be only that kind of continuity which is observed in dissociative changes generally. Although statistical analysis may support the conclusion that the gaseous state and that which obtains in a dilute solution are comparable, a consideration of the phenomena in the light of our knowledge of intermolecular relationships cannot at present be held to justify any such assumption; how can it be permissible, in fact, to compare the approximate truth of the laws of Boyle and Gay-Lussac with Raoult's if in solution an all-important part be played by a factor—the solvent—which, in the case of gases, may be left almost entirely out of consideration; and if water be not a neutral substance and the phenomena of dissolution are, as many believe, of a high order of complexity.

The regular and rational results which are obtained on applying the Raoult methods to dilute solutions of substances of known molecular weight are undoubtedly very striking and likely to carry conviction to many minds that the methods are of universal application; but other equally striking coincidences have been observed. Thus it is highly remarkable that the hydroxides generally—in dilute solutions be it observed—have the same heat of neutralisation. This illustration is of special moment, for if we consider the supposed interagents alone and disregard the solvent as a chemical agent, it is inconceivable that such should be the case; the result must be in some way a consequence of a higher law not yet clearly perceptible through the haze of complexity which so enshrouds the phenomena of chemical change in solution. It cannot be doubted that the constancy is conditioned by the presence of water in large relative quantity, as most irregular and dissimilar results are obtained if the comparison be made for any other than dilute solutions, just as in the case of the Raoult freezing method (cf. Beckmann, *Zeit. Phys. Chem.*, 1888, 638 and 715).

If the argument here advanced be admitted, it follows that not only the molecular weight of a substance but also its *specific effect* must be taken into account; and this is undoubtedly the case. It is well known that acids and metallic salts, and indeed electrolytes generally, give abnormal results; they produce too great an effect. Arrhenius has suggested that such compounds are present in solution in a more or less dissociated condition—dissociated into their "*ions*;" that, in fact, such solutions contain a greater number of active molecules than are usually supposed to be present. Allowing for this increase in a manner which he has pointed out, "normal" results are obtained in place of the impossibly low molecular weights which result from the direct reduction of the experimental values. But if we are to accept this view, we must admit that water is a neutral substance, and that it plays no active part in electrolysis; in other words, such a conclusion directly involves the acceptation of a particular hypothesis as to the nature of electrolysis. The arguments on which this hypothesis is based, however, are mostly cases of circular reasoning, and there are many facts which apparently cannot be satisfactorily accounted for by it (cf. *B. A. Report*, 1888, 356). The one argument in favour of the dissociation hypothesis which is generally regarded as all-sufficient—the argument originally advanced by Clausius, that any E.M.F., however small it may be, produces sensible electrolysis, is one of which it would be premature to accept any explanation as final in our entire ignorance of the inner mechanism of electrical actions—while the electric current is an unsolved mystery, as was happily observed by Professor Rowland in a recent lecture—especially as there are electricians who are of opinion that the Clausius hypothesis is not necessarily the only possible solution, although at present unable to suggest a more satisfactory one. But not only is the explanation of electrolysis which is usually given of a purely "mechanical" nature, and incompatible, therefore, with the view that the solvent plays an active part; it is open also to the objection that in framing it attention has been paid too exclusively to a certain limited number of phenomena, and that the bearing of the facts of chemistry generally as these present themselves to the mind of the chemist has been insufficiently considered. It is probable that this will soon cease to be the case, as signs are not wanting that it will ere long be recognised that chemical changes are essentially electrolytic phenomena, and that we may expect to witness the rehabilitation of Faraday's view of 1834 of "the identity of the force constituting the voltaic current or electrolytic agent with that which holds the elements of electrolytes together, or, in other words, with chemical affinity."

Although it may be urged that the method which Arrhenius has introduced of correcting the results obtained in the case of electrolytes is based on an incorrect interpretation of the phenomena, it does not follow that his method is necessarily a faulty one: on the contrary. Practically the method involves nothing more than the recognition of the fact that it is possible to determine with a close approach to accuracy, and to allow for, the *specific effect* which a compound exercises. This would seem to be the case. Thus Ostwald's experiments show that in the case of acids, for example, in seeking to determine the order of activity in which these may be arranged, practically the same result is arrived at, the order deduced being very similar when very diverse properties are made the subject of study. Molecular weight does not come into evidence as a determining cause of position in such a series, compounds such as hydrogen chloride, bromide, and iodide occurring together and almost at the head of the scale of activity, while hydrogen fluoride is found low down in the series. The compounds in such a series afford "abnormal" values when examined by the Raoult methods in dilute solutions owing to their exercising a greater effect than is produced by compounds which give "normal" values; the extent to which the effect produced is in excess depends on the position in the series, and if proper allowance be made on this assumption a "normal" value is necessarily obtained, *i.e.*, a value consonant with the view which on general grounds we are led to form as to what would be the composition of the molecule of the substance if it were obtained in the gaseous state. But it has yet to be proved that such "corrected normal" values, and those directly found for neutral compounds which can be gasified, uniformly represent the true molecular weights of the dissolved substances, and not merely the weights of their fundamental molecules (cf. *Proceedings*, 1889, 42).

Whereas in dilute solutions an excessive effect is often produced which would lead to the molecular weight being under-estimated if the result were at once accepted, in the case of concentrated solutions a contrary result is frequently encountered, corresponding to more or less exaggerated estimates of the molecular weight; thus the effect produced by alcohol, for example, in a 32·5 per cent solution is such as apparently to correspond to a molecular weight of 318 (Beckmann). It is not difficult to explain this result on the mechanical hypothesis of the nature of solutions, and still less difficult on the assumption that dissolution is in the main a chemical process: inasmuch as in concentrated solutions less opportunity is given for the molecules of the dissolved substance individually to exercise their specific heat; inasmuch as molecular aggregates are more likely to persist; and inasmuch as the solvent may consist no longer of the substance ostensibly employed as solvent, but in part, at least, of a compound of solvent and dissolved substance. The reduction of the specific effect, and the consequent exaggeration of the molecular weight in the cases here contemplated, may be said to be due to inter- if not to extra molecular compensation.

But it is also conceivable that intra-molecular compensation may take place, and that there may be compounds, the existence of which is not to be foreseen on the dissociation hypothesis, which exercise not an excessive but an inferior effect. The molecular weight of such compounds would necessarily be over-estimated by the application of the Raoult methods. Benzene and thiophen may be cited as mere illustrations of what is meant by internal compensation; benzene, it is well known, does not manifest the activity of a "triethylenic" compound, and evidently, in some manner not clearly understood, the six "surplus" affinities of the six carbon atoms internally neutralise or compensate each other; in thiophen the sulphur appears to function only as a dyad, manifesting no tendency whatever to exhibit a higher valency in the manner so characteristic of sulphur in open chain compounds: the inclusion of the sulphur in the chain in this case, therefore, involves a marked diminution in its activity.

It may be suggested that probably colloids generally are compounds of inferior activity, such as are contemplated on the view here put forward. It is well known that they diffuse with extreme slowness (*cf. Nature*, xxxv., 598), and they are as a class very inert substances, the vapour-pressures of their aqueous solutions, for example, being almost if not the same as those of water alone at the same temperatures. The results recently brought forward by Brown and Morris for carbohydrates are of great interest, but it may be doubted whether they do more than confirm the views previously held with regard to the relative complexity of the several compounds. The same remark applies to the observations of Gladstone and Hibbert on caoutchouc. The fundamental molecule of a glucose must contain at least 6 carbon atoms, and that of a saccharon (any member of the cane-sugar group) 12; that of an amylin (or dextrin) therefore most probably contains at least 24 carbon atoms. A variety of *amyloins* might well result from the conjunction of amylon (maltose) and amylin molecules in various proportions: maltodextrin,—

$$C_{12}H_{22}O_{11}\cdot 2C_{12}H_{20}O_{12} = C_{12}H_{22}O_{11}\cdot C_{24}H_{40}O_{20};$$

inulin,—

$$2C_{12}H_{22}O_{11}\cdot 4C_{12}H_{20}O_{10} = 2C_{12}H_{22}O_{11}\cdot 2C_{24}H_{40}O_{20};$$

and amylodextrin,—

$$C_{12}H_{12}O_{11}\cdot 6C_{12}H_{20}O_{10} = C_{12}H_{22}O_{11}\cdot 3C_{24}H_{40}O_{20},$$

representing these by the formula assigned to them by Brown and Morris, are apparently such compounds. By duplication of the molecule and withdrawal of the elements of water from such amyloins, "higher dextrins" might be formed which would still be compounds of moderate molecular weight; and even simpler compounds would result if the amyloins were merely to lose the elements of water. Compounds thus formed would undoubtedly be less active than the parent carbohydrates, owing to the "cancelling" of the hydroxyl-groups; and it may well be that they would exercise an inferior effect in solution, and one such as is observed in the case of colloids.

It is undoubted that by the application of the Raoult methods a number of most interesting facts have been elucidated, which it is impossible and unnecessary to deny, but it is equally certain that we are only called on to make a rational use of them, and that slavish submission to the facts cannot be demanded. Those who directly accept the conclusions which are drawn, perhaps, have hardly realised what is involved, viz., adherence to the view that in a dilute aqueous solution of hydrogen chloride, for example as much as 90 per cent of the chloride is present, not as such, but in the form of *free hydrogen and chlorine atoms:* such a conclusion may enable certain mathematical problems to be solved in an apparently satisfactory manner, but it is hardly one which a chemist's common sense would lead him to accept orthwith, in the absence of any explanation accounting for so extraordinary a difference between a dissolved substance at a low temperature and the same substance in the gaseous state at a high temperature. Attention may also be directed to the contradiction involved in the assumption that hydrogen chloride, although not appreciably dissociated when heated alone at 1500° in porcelain (Crafts and Meier) undergoes almost complete dissociation when dissolved in water, whereas nitrogen peroxide, according to Ramsay's experiments, exists in solution as N_2O_4, notwithstanding that it cannot be gasified unchanged, and is almost entirely resolved into NO_2 molecules at a temperature of about 200°.

Discussion.

Dr. Gladstone defended Raoult's freezing method, relying on the numerous coincidences between its indications and those afforded by vapour-density determinations. In illustration he referred to the polymeric C_5H_8 hydrocarbons. Mr. Hibbert and he had found that each of these, when dissolved in benzene, gave a freezing-point indicating an analogous molecular composition in the gaseous and dissolved condition. The conclusion from the small lowering produced by colloids that they have a very complex molecule is only in accordance with what has been long believed on chemical grounds. No doubt there are discrepancies and difficulties; but a careful consideration of these must serve to improve our knowledge of chemical and physical theory.

Mr. Hibbert said, that in applying Raoult's method, he had found it advantageous to surround the freezing vessel with an air chamber. The freezing-point was then more definite.

The contention of Dr. Armstrong against the applicability of Raoult's method to colloid substances was based on objections to the dissociation theory of electrolysis. It might be true that the only argument in favour of that theory was the fact that the smallest electromotive force was able to produce decomposition in an electrolyte, but the argument was a very strong one, and commanded the assent of nearly every physicist in Europe. With reference to the effect of colloids on boiling-point, &c., the question was whether they did or did not produce a real alteration. Recent researches seemed in favour of a positive result.

66. "*The Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen.*" By J. H. Gladstone, Ph.D., F.R.S., and W. H. Perkin, Ph.D., F.R.S.

The substances containing nitrogen, the magnetic rotation of which was described in Dr. Perkin's recent paper, have been examined by Dr. Gladstone with reference to their refraction and dispersion. The result is given in a table in which the molecular magnetic rotation, molecular refraction, and molecular dispersion for 41 substances are placed in parallel columns with a view of drawing attention to the general correspondence that exists between these three different properties of the substances in question; a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance. Each property is governed by the following primary law. The molecular magnetic rotation, refraction, or dispersion of a compound body is the sum of the atomic magnetic rotation, refraction, or dispersion of its constituents. The values which have been deduced under this primary law are, however, subject to large modifications dependent upon differences in the structure of the compound.

The paper shows that when a change occurs in one property, it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent; in fact, the variations in the magnetic rotation are usually greater than those in the dispersion, and these again are much more marked than in the refraction.

Eight sets of comparisons are given, each showing the correspondence in a different way:—

1. Compound ammonias. Ethylamines and propylamines, showing for each additional substitution a continuous augmentation of the value,

2. Hydrochlorides of the ethylamines, showing for each substitution a value smaller than the normal.

3. Methylanilines, showing a greatly increased value for CH_2.

4. Unsaturated compounds, allylamine, pyridine, and aniline, showing a great increase upon the values for saturated compounds.

5. Propylamine compared with propionitril and trimethylene cyanide, showing two different values for nitrogen.

6. Nitric ethers, showing normal values for each CH_2, except the first.

7. Isobutyl nitrite and nitrate, showing the diminution of the nitrogen value with change of valency.

8. Acids and their ammonium salts, showing a superior value for acids in aqueous solution, and its continuance or partial disappearance on combination with nitrogen bases.

Apparent exceptions are mentioned, but the following is the general conclusion :—

It may be laid down as generally if not always true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The general drift of the old comparison appears to lead irresistibly to the conclusion that we have here another close relationship between electromagnetism and the velocity of light.

(To be continued).

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—In reference to Mr. T. Bruce Warren's letter in the Chemical News, vol. lx., p. 36, allow me to point out that our registered name "Thiocamf" applies specially to a disinfectant compound in which the sulphur dioxide and camphor liquid is the solvent for other powerful disinfectants.—I am, &c.,

The Secretary,
Thiocamf Disinfectant Co.

Thiocamf Disinfectant Company,
5, Lower Merrion Street. Dublin,
July 22, 1889.

The Detection of Sugar in the Commercial Extract of Logwood. — Otto Schweissinger (*Pharm. Central-halle*).—From 2 to 5 grms. of the extract are dissolved in 50 c.c. water, mixed with 10 c.c. basic lead acetate, well shaken, and, after standing for a short time, poured upon a dry filter. So much of the liquid runs through that it can be at once polarised in a tube 100 m.m. in length. Filtrates from pure extracts deflect the plane of polarisation not at all or but little, certainly not to the right. The entire filtrate (25 to 30 c.c.) is mixed with so much lead chloride that the lead is precipitated as chloride and about 0·5 grm. hydrochloric acid remains in excess. The acid liquid is heated in a reflux condenser for half an hour and let cool. The crystals of lead chloride are disregarded and the liquid is neutralised with sodium carbonate, filtered, and titrated with Fehling's liquid. Two pure samples, when thus treated, showed no sugar, three suspicious ones respectively 6, 7, and 8 per cent, and a grossly adulterated sample 20 per cent.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 2, July 8, 1889.

Solubility of Carbonic Acid Gas in Chloroform.—M. Woukoloff.—Carbonic acid, when dissolving in chloroform at 13°, does not follow strictly the law of Dalton, but the deviations are very small, as we have also seen for carbon disulphide.

Solidification of Nitrous Acid.—Fl. Birhans.—To solidify anhydrous nitrous acid, though still containing small quantities of hyponitric acid, there is required a temperature of −52° to −54°, obtained by the evaporation of methyl chloride in a current of dry air. To obtain anhydrous nitrous acid free from hyponitric acid, the author has operated similarly to Fritsche, but at a lower temperature. It forms a fine blue liquid, which was solidified only by the cold produced by a mixture of methyl chloride and carbonic acid in the flocculent state. This mixture, according to the experiments of MM. Cailletet and Colardeau, lowers the temperature to −82°.

On the Barium Cobaltites, and on the Existence of a Cobalt Dioxide having an Acid Function.—G. Rousseau.—The author's experiments show the existence of a cobaltous acid analogous to manganous acid, but feebler. The maximum stability of barium manganite lies about 1100°. The compound is dissociated either at higher or lower temperatures.

A Copper Oxybromide, analogous to Altacamite.—Et. Brun.—A solution of potassium bromide, saturated in the cold with cuprous bromide, deposits, when left in contact with the air, a precipitate which, after being freed by decantation from the supernatant liquid, and being repeatedly washed with a solution of potassium bromide, appears in the form of small deep green crystals, insoluble in water, but soluble in dilute acids and in ammonia. At 240° to 250° this compound is entirely destroyed, and the residue, on treatment with water, gives off copper chloride, which dissolves, whilst copper oxide remains as a black powder.

New Derivatives of Camphor.—M. Haller.—This memoir is not susceptible of useful abridgment.

On the Dioxyphosphinic Acids.—J. Ville.—The aldehyds unite directly with hypophosphorous acid and yield trivalent and monobasic acids. These acids have no reductive action upon ammoniacal silver nitrate and upon copper sulphate; they have a tendency to become split up, setting at liberty the aldehyd from which they are derived.

Researches on the Purple produced by Purpura Lapillus.—Augustin Letellier.—This mollusk is very common on the shores of Bretagne, and was formerly used by the Bretons in dyeing. The colour is generated in a yellowish white band. The purple is, in fact, produced by three substances, one of them yellow and not photogenic, whilst the two others turn quickly to a blue and a carmine red under the influence of the sun's rays. The yellow substance forms crystals similar to those of uric acid. The substance is soluble in potassa, whence it may be precipitated by weak acids. The two photogenic substances are the one apple-green and the other ash-green. The crystals of the former have the appearance of magenta; light quickly renders them opaque and deep blue. They dissolve sparingly in water but readily in chloroform and in petroleum ether. The crystals of the third body are very soluble in water. They become red, violet, or carmine on exposure to light, according to their degree of purity. To prepare even a very small

quantity of these three bodies the bands must be detached from several hundred specimens of *Purpura* dried at the common temperature in a vacuum over sulphuric acid. When dried they are powdered, treated with ether, which is let evaporate, and the residue is taken up in potassa, which dissolves the fats and the yellow matter. The whole is filtered. The filtrate, on the addition of acetic acid, deposits the yellow matter. The green residue on the filter is treated with chloroform, which dissolves the ash-green substance more readily than the apple-green. If petroleum ether is used the apple-green crystals dissolve more rapidly. All these operations must take place in the dark. When once formed the purple is an impalpable powder, insoluble in the ordinary solvents. Nitric acid and chlorine-water destroy it; sulphuric acid converts it into an emerald green substance, which, on the addition of water, becomes an indigo-blue liquid, but in time the matter becomes carbonised. The action of light upon the purple matter suspended in chloroform is curious. It extinguishes the less refrangible red rays, absorbs the yellow, the most refrangible part of the blue, all the indigo, and all the violet. We have a continuous spectrum formed of a dirty orange-red band, contiguous by irradiation with a broad green band edged with blue. The yellow is so well absorbed that it is not perceived. The only radiations which pass through are those comprised between 720 and 613, 535 and 490. The purple seems to take its rise by a process of reduction. The purpurigenous matter, if treated with oxygenated water, hypochlorous acid, or potassium dichromate, remains intact, but in presence of sodium amalgam it turns to a reddish purple.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 2.

Determination of Theine in the Teas of Comerce.m—Hilger (*Archiv der Pharmacie*) exhausts 10 to 20 grms. of tea repeatedly with boiling water, precipitates the filtered extract with basic lead acetate, avoiding a large excess, filters off the precipitate, washes with hot water, and decomposes with hydrogen sulphide. The filtrate is evaporated to dryness after the addition of wash-sand and a little lime or magnesia, and the residue is extracted perfectly with boiling chloroform in Soxhlet's apparatus. This extract yields a slightly coloured residue, which, after drying for three hours at 100°, is weighed, and may be obtained perfectly colourless by re-crystallisation from alcohol or boiling water.

Determination of Uric Acid.— A. Hermann (*Zeit. Physiolog. Chemie*) has examined Haycraft's method, and concludes that, though the results are too high, it may be useful in clinical examinations.

The Spectrum of Methæmoglobine.— H. Bertin-Sans.—From the *Comptes Rendus*.

The Spectrum of Reduced Hæmoglobine.—L. Hermann (*Pflüger's Archiv*).—In the broad absorption-band between D and E near the edge towards the red there is a narrow rather lighter interval. Hence the absorption-band in a rather narrow spectrum appears to consist of a narrow absorption stripe near the line D and a broad one extending towards E.

The Spectroscopic Demonstration of Traces of Blood in Urine and in Other Liquids.—C. H. Wolff (*Pharm. Central-halle*) puts 30 to 60 c.c. of the urine in question in a capacious test-tube with one-tenth its volume of a three per cent solution of zinc acetate and heats it in the water-bath until the precipitate collects together and settles so far that the supernatant liquid can be decanted clear. The deposit is collected upon a small filter, washed, and covered with a few c.c. ammonia. The precipitate dissolves and the solution is let run into a test-tube 10 c.m. in length and 12 m.m. in width and made up to 4 to 5 c.c. by washing the filter. The filtrate is covered with a few c.c. of benzine, to exclude air, and mixed with 2 drops of a solution of ferrous sulphate containing tartaric acid (1 part each of tartaric acid and ferrous sulphate in 10 parts water), whereby the hæmatine is reduced and may be examined with the spectroscope. The characteristic absorption-band in the green,—

$$a = \lambda\, 564—547,$$

can be seen even in the greatest dilution.

Densimetric Determination of Albumen in Animal Fluids. — Huppert and Záhor have examined the applicability of this procedure as proposed by Bornhardt.

MISCELLANEOUS.

London Sewage.—In view of the difficult question of the disposal of London sewage receiving the attention of the London County Council shortly, Sir H. Roscoe, M.P., has issued a statement of the position of affairs. Sir Henry has come to the conclusion that the proposal of the Board of Works for the disposal of the sewage was based on false principles—first, as regards the addition of lime and iron in the proportions recommended; second, as regards the addition of manganate of soda to the effluent, after precipitation, in the quantities suggested; third, as regards the formation of underground settling tanks at Barking and Crossness; fourth, as regards pumping the sludge into tank steamers and sending it out to sea. On this £1.013,786 had been spent from 1884—88 inclusive. Sir H. Roscoe suggests that an engineer of high eminence, and a chemist of like position, should at once be appointed to reconsider the whole question.— *Gravesend and Dartford Reporter*.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Chemical Manufacturers.—J. M. wishes to learn the publisher of a work containing a list of chemical manufacturers.

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THE CHEMICAL NEWS.

Vol. LX. No. 1549.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

Continued from p. 41).

The Yttrium Group.

Yttrium—the old yttrium—proves now to be not a simple element, but a highly complex substance. I have come to the conclusion that it may be split up certainly into five and probably into six constituents. Its phosphorescence spectrum is shown in Fig. 16, and the different bands are designated by certain letters. Fig. 17 shows the simple spectra of the separate components into which yttria can be separated by fractionation. If we take these constituents in the order of their approximate basicity — the chemical analogue of refrangibility — the lowest of these constituents gives a deep blue band, Gα; then follows a strong citron band, Gδ, which increases in sharpness until it may be called a line; then a red band, Gζ; then a deeper red band, Gη; and lastly a close pair of greenish blue lines, Gβ. Following these are frequently seen Gε, Gγ, and Gθ, the yellow, green, and red components of samarium, Fig. 19.

As the result of many years' work and several thousand fractionations of old yttria, I exhibit the series of 19 phosphorescence spectra shown on Diagram 28. The centre spectrum, marked J, is approximately that given by the crude earth, although this differs slightly according to the mineral from which it is extracted. After a time, fractionation splits the earth J into two earths, I and K, giving slightly different spectra. Fractionating I gives H and J, whilst K on fractionation yields J and L. The state of separation to which the meta-elements of the samarskite earths may be brought after many years' work is seen by the series of 19 spectra selected to illustrate the progress of the work. It must not, however, be thought that there is so great a difference between any two adjacent spectra as is here shown. To make the diagram more accurately represent what actually occurs in the laboratory it would be necessary to place between each of these 19 spectra about 1000 intermediate spectra.

Beginning at the extreme red it will be seen that a strong band at λ 647 ($1/\lambda^2$ 239) is of maximum intensity from G to K, when it rapidly disappears and is not seen beyond C and N. The meta-element giving this band I have called Gη. The next band in the red λ 639 ($1/\lambda^2$ 245), is at its maximum at A or even above, while it fades out between K and L. The next band at λ 619 ($1/\lambda^2$ 261) has its maximum between I and O, fading out rapidly below, but being more persistent above. The meta-element to which this band is due I have called Gζ. I next come to an extremely sharp band at λ 609 ($1/\lambda^2$ 269), which appears to belong to an earth absent in gadolinite, and present in samarskite and a few other minerals. Its greatest brilliancy is between E and K, dying away rapidly on either side. This meta-element I have called Sδ. A double orange band follows, and there are indications that its two components are separable, although they must be very closely associated. The maximum brightness of the first component, λ 603 ($1/\lambda^2$ 275), extends from O to the top of the diagram. The second component, λ 597 ($1/\lambda^2$ 280), begins to lose brilliancy about G, and, like its companion, is at its greatest brightness at the highest spectrum shown on the diagram. This band has been almost isolated in a specimen of crude lanthana. I have called its meta-element Gα.

The next band in order is the citron or Gδ band, λ 574 ($1/\lambda^2$ 303·5), the most prominent in the spectrum of old yttrium. This band extends with almost undiminished sharpness and brilliancy from G to S; above G it fades out rapidly, and from D upwards it is absent. Following the citron band is a double green band. This, like the orange band just described, is separable into two components. The first, at λ 568 ($1/\lambda^2$ 310), is almost absent in A, attains its maximum in about D, and fades out entirely at K. The second component of this green pair, λ 563 ($1/\lambda^2$ 315), is at its maximum at A and above, and extends only to H. The meta-element giving rise to this pair I have called Gγ. Next in order comes a pair of bright green bands. The two components λ 550, 541 ($1/\lambda^2$ 331, 342) have not yet shown signs of dividing. The first appearance of this double band is at B, it attains its maximum at about E, and continues with almost undiminished brightness to Q. The body giving this double green band is the most persistent of all the meta-elements of these earths. I have provisionally called it Gβ.

After a dark interval a broad, hazy, double blue band is seen, having its centre at λ 482 ($1/\lambda^2$ 430·5). This band, first appearing at about F, increases in brightness down to the last fraction at S. Its meta-element is called Gα. Lastly, at λ 456 ($1/\lambda^2$ 481), is seen a deep violet band, coming in first at Q, and getting brighter as we get lower down the fractionations. This band is of extraordinary brilliancy in some samples of ytterbia, but as it is absent in a specimen of ytterbia from Nilson, said by him to be perfectly pure, it is probably due to some other new body which I have therefore named provisionally Sγ.

Although, for economy of space, it is inconvenient to represent a longer series than is here shown, my fractionations have been pushed far beyond the limits shown on the diagram. Fractions above A and below S give ample evidence that the process of differentiation has not reached its utmost limit.

On the left of the diagram, Fig. 28, I have attached chemical symbols to some of the spectra. Thus the top spectrum, A, is the one shown by samarium. At D is the spectrum given by Marignac's Yα or gadolinium. At H is seen the spectrum of mosandrum, and at L is shown the spectrum given by what would ordinarily be called pure yttrium. A study of this diagram will, I think, convince any impartial observer that the lessons it conveys fully bear out my contention that samarium, gadolinium, mosandrum, and yttrium, are not actual chemical elements, but are compounded of certain simpler bodies which may conveniently be called "meta-elements."

A possible explanation of the existence and nature of the new bodies into which "old yttrium" has been split up, and of parallel cases which will doubtless be found on closer examination, is this. Our notions of a chemical element must be enlarged; hitherto the elemental molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element is certainly more complicated than has hitherto been supposed. We may reasonably suspect that between the molecules we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there intervene sub-molecules, sub-aggregates of atoms, or meta-elements, differing from each other according to the position they occupy in the very complex structure known as "old yttrium."

The arguments in favour of the different theories are

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

as yet not unequally balanced. But the assumption of compound molecules will perhaps account for the facts, and thus legitimate itself as a good working hypothesis, whilst it does not seem so bold an alternative as the assumption of eight or nine new elements.

The history of the examination of the rare earths and of its results would lack completeness and intelligibility did I not refer to the views taken by my distinguished friend M. Lecoq de Boisbaudran.

In a communication to the Academy of Sciences this eminent chemist says (*Compt. Rend.*, c., 1437): "It is a singular fact that the position of the phosphorescence bands observed by Mr. Crookes with very pure compounds of yttrium are sufficiently near those which I, on my part, have obtained with the hydrochloric solutions of earths separated as far as possible from yttria, chemically as well as spectroscopically. My reversion spectrum cannot, I think, be attributed to yttrium, for on the one hand it is seen *brilliantly* with products which give no trace of yttrium rays with the direct spark, and on the other hand, I have found it impossible to obtain it sharply from certain earths extremely rich in yttria."

M. de Boisbaudran further states in a note:—"This spectrum (*i.e.*, the one which he had just described) is now recognised as being identical with that which is ascribed to pure yttria by Mr. Crookes, and which this *savant* obtained under experimental conditions very different from mine. Nevertheless, my latest observations, as well as earlier ones, lead to the conclusion that yttria is not the cause of the spectrum bands observed. In my fractionations the phosphorescence spectrum gradually gets weaker as I advance towards the yttria end. With almost pure yttria the phosphorescent bands show themselves faintly or not at all, whilst they are brilliant with the earths which do not give by the direct spark the rays of yttrium to any appreciable extent."

It will, I think, appear that the issue between myself and M. de Boisbaudran turns on the question: What is yttria? To what substance can this name be legitimately given? A short time ago the name conveyed to all chemists only one meaning, perfectly definite and undisputed. I have received specimens of yttria from M. de Marignac, considered by him to be purer than any which had ever been previously prepared; from Professor Clève (called by him *purissimum*); and from M. de Boisbaudran, which he pronounces to be yttria "scarcely soiled by traces of other earths." Along with these I have specimens prepared by myself and purified up to the highest point known. A very short time ago every living chemist would have called these samples "yttria." Moreover, they all give my phosphorescence spectrum *in vacuo* with such intensity that such phosphorescence cannot be rationally ascribed to slight traces of impurities.

This substance, like other chemists, I formerly called "yttria," but since its complex nature has been ascertained I speak of it as "*old* yttria."

M. de Boisbaudran, however, inadvertently uses the word in a manner not quite free from ambiguity. By "yttria," I repeat that I mean now, and have always meant, the yttria of Clève, of Marignac, and of all chemists up to the beginning of the year 1886, the yttria whose metallic base has the approximate atomic weight of 89. M. de Boisbaudran at one time writes as if our meanings were identical: "It is certain," he says, "that my earth, very rich in yttria, gives a beautiful spectrum in the vacuum tube." Again he informs me, "M. Becquerel has recently examined my earths A and B in ultra-violet light, and has obtained results analogous to yours; that is to say, the earth rich in yttria has generally shone brighter than the other." The "earth A" here spoken of gives my phosphorescent spectrum with wonderful brilliancy, and is the one described above by M. de Boisbaudran as "yttria scarcely soiled by traces of other earths." This yttria, my distinguished friend goes on to say, "is the same as that of Clève and Marignac, varying only in slight impurities, Marignac's being perhaps the purer." So far then we agree in the meaning to be attached to the word "yttria."

But at other times M. de Boisbaudran gives the name "yttria" to an earth of quite distinct properties, to an earth he has obtained in most minute quantities after months of reiterated fractionation, which gives *no* spectrum in the vacuum tube. Here, therefore, we have the name "yttria" applied to two distinct substances, the one giving a brilliant phosphorescence spectrum, and the other giving none at all, surely a misleading ambiguity. Moreover, I am constrained to question the propriety of my friend's use of the designation "yttria" in the latter sense. Quite recently (*Compt. Rend.*, cviii., 166, January 28, 1889) M. de Boisbaudran has defined his "yttria" as an earth, whether simple or complex, having a characteristic spark spectrum, but not giving a phosphorescence spectrum in the radiant matter tube or by his process of reversion, and having an atomic weight of nearly 89 for its metal.

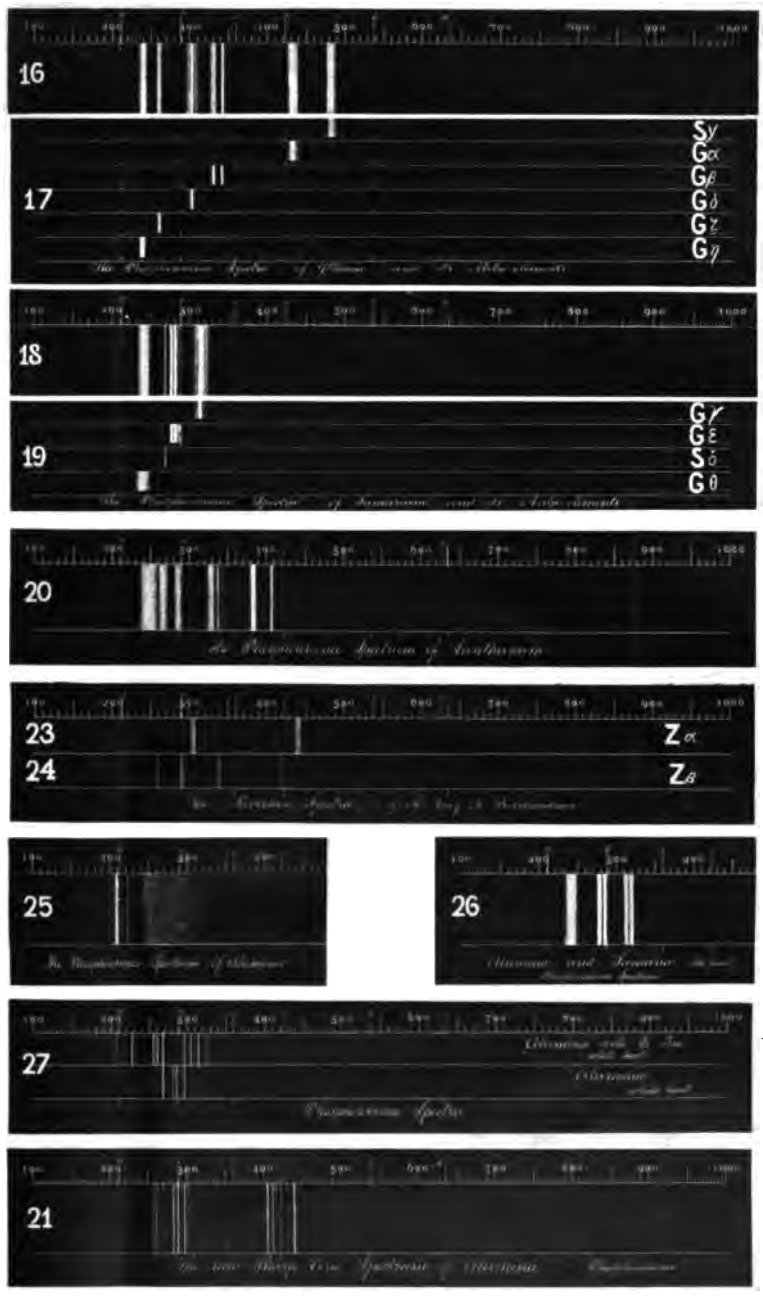
Why should this non-phosphorescent earth deserve the name of elemental yttria? Why may we not just as well allot the name to some one or other of the phosphorescing earths which M. de Boisbaudran brands as impurities? It seems to me that to refine away the most characteristic attributes of a body, to call the *caput mortuum* by the original name, and pronounce everything else as "impurity," is a departure from the recognised principles of scientific reasoning and practice which it is a duty to protest against.

I have just mentioned that the earth heretofore called yttria and supposed to be simple has been split up into a number of simpler bodies. Now these constituents of the old yttria are not *impurities* in yttria any more than praseodymium and neodymium are impurities in didymium. They proceed from a real splitting up of the yttrium molecule into its components, and when this process is completed the old "yttria" has disappeared. If these newly discovered components on further examination should be found worthy to take the rank of elements, I think as first discoverer, I am entitled by the custom prevailing among men of science, to name them. For the present, and until their investigation is more advanced, I designate them by provisional symbols. One of the most distinct characteristics of "old yttria" is its very definite spark spectrum. To which of its components this spark spectrum belongs I am not yet able to say. It is possible that the particular component to which the spark spectrum is due yields no phosphorescent spectrum. It is also possible that the spark spectrum, like "old yttria," may prove to be compound, and then the well-known lines it contains will have to be shared between two or more of the newly-discovered bodies. I wish emphatically to re-state that at present no single component of old yttria can lawfully lay claim to what may be called the paternal name; and it seems to me that in the present state of the question no one is entitled to call one of the new bodies "yttria," and to characterise the remainder as impurities.

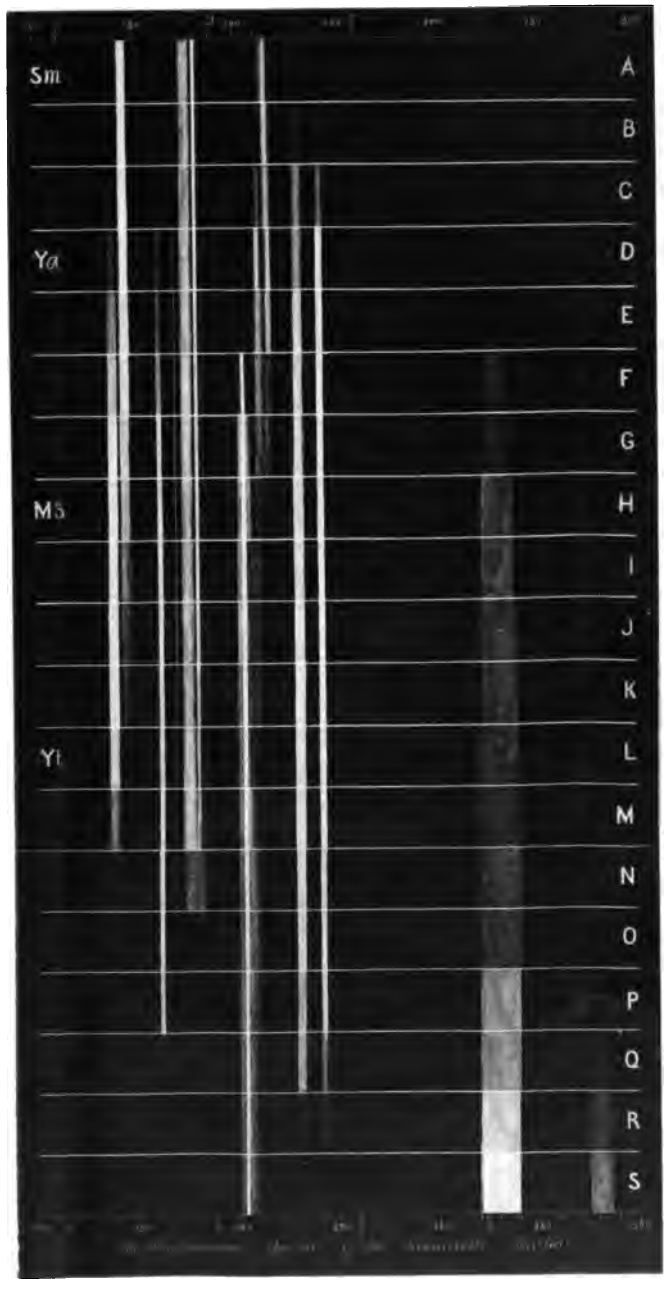
I regret to add that a misunderstanding exists between M. de Boisbaudran and myself. In a memoir presented to the Academy of Sciences on January 28th of the present year my distinguished colleague shows he completely misapprehends my position, and he so far misinterprets me as to make me say that the gadolinia or Ys of M. de Marignac is a mixture of 61 parts of yttria and 39 parts of samaria!

But what is the fact? So far back as June 9th, 1886, I put it on record (*Proc. Roy. Soc.*, xl., 502) that "Ys is composed of the following band-forming bodies:—λ [541—549], [564], [597], [609], [619], together with a little samarium. Calling samarium an impurity, it is thus seen that gadolinium is composed of at least four simple bodies."

Again in a paper entitled "What is Yttria?" I wrote (Chem. News, liv., 39, July 23, 1886)—



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.

"Gadolinium is composed of at least four simpler bodies, Gβ, Gγ, Sâ, and Gζ; the pair of green lines [λ 541 and λ 449, mean 545], being the strongest feature in its spectrum, may be characteristic of gadolinium."

"M. de Boisbaudran says:—'Mr. Crookes appears to attribute to gadolinium the double green band.' This is scarcely accurate; I did not ascribe the double green band to gadolinium, but finding by my test that the *so-called* gadolinium was a compound body, the earth Gβ being its strongest component, I proposed to attach the name of gadolinium to Gβ rather than give it a new name, and thus multiply names unnecessarily."

Thus in 1886 I corrected the error which M. de Boisbaudran now repeats.

Again, I said that the work of fractionating this mixture, "*for its completion*, would occupy a space of time in comparison with which the life of man is all too brief"—a statement transformed into the assertion that to separate yttria and samaria—a relatively easy task—would take more than a life-time.

M. de Boisbaudran's misconception is the more striking since in a foot-note he gives correctly my very words from my "Address to the Chemical Section of the British Association," in 1886, and from the "Genesis of the Elements." How he can have mistaken my meaning is a mystery, as he is an excellent English scholar. Certainly any reader of the *Comptes Rendus* who understands English will at once see that there is no foundation for M. de Boisbaudran's criticism.

(To be continued).

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

(Concluded from p. 45).

B. *Insoluble Form of the Foregoing.*

The solution of the blue product just described is influenced in a remarkable way by the addition of almost any neutral substance. So far I have not found any that does not precipitate it. No only saline solutions do this, but even a solution of gum arabic.

Neutral salts may precipitate the silver in either a soluble or an insoluble form. Alkaline sulphates, nitrates, and citrates throw down the soluble form; magnesium sulphate, cupric sulphate, ferrous sulphate, nickel sulphate, potassium bichromate and ferrocyanide, barium nitrate, even silver nitrate, and other salts throw down a perfectly insoluble form. The soluble form constitutes a blue or bluish black precipitate; the insoluble, a purple brown, which, by repeated washing, by decantation, or otherwise, continually darkens.

What is very curious is that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution, potassium and sodium sulphate produce a yellowish red solution, and ammonium sulphate a red one. None of these solutions has the same blood-red colour as the original solution; the form of silver seems to change with the slightest change of condition.

The solutions used must be extremely dilute, otherwise the silver, though rendered soluble in pure water by them, will not dissolve in the solution itself, a singular complication of effects. So that if a moderately strong solution of one of the above substances is poured over the insoluble silver substance it does not dissolve, but by pouring off the saline solution and replacing it with pure water, the substance now dissolves readily. The insoluble substance is also readily soluble in ammonia. The solution has a fine red colour, and not the yellowish red of the sodium sulphate solution.

Most neutral salts act in one or other of the ways just described, precipitating the solution of the blue substance A in either the soluble or the insoluble form, the latter so uble in ammonia, but sodium nitrite is an exception; its solution effects an entire change and renders the substance wholly insoluble, probably re-converting it to normal silver.

Sometimes the substance will spontaneously pass into a soluble form. A specimen, rendered insoluble by precipitation with ferrous sulphate, after much washing began to run through, not only as a suspension, which often happens, but as a solution, clearing itself after a day or two of insoluble portions, and furnishing a rose-red solution. I have kept this solution in a corked vial for eight months, during which time it has remained unchanged.

The general properties of this substance can be much better observed in the thin films obtained by brushing the moist substance over paper than in the lumps. The films thus obtained are bright greenish metallic, and this green evidently results from a mixture of blue and yellow, as in some lights the blue, in others the yellow, is most evident. When these films are examined by light reflected from them at a large incidence with the normal and a Nicol's prism, or an achromatised prism of calc-spar is interposed between the film and the eye, it becomes at once apparent that the blue and yellow light are oppositely polarised. The yellow light is polarised in the plane of incidence, the blue light perpendicularly to that plane. All specimens show the yellow light, but the quantity of blue light is very variable and is directly connected with the amount of washing applied to the precipitate. The more it is washed the more the yellow predominates. To see the blue form in its full beauty, a little of the red solution may be precipitated with a very little magnesium or aluminium sulphate and be thrown on a filter. As soon as the liquid has drained off and, without any washing, the deep bronze-coloured substance is to be brushed over paper. On drying it has all the appearance of a bright blue metal with a remarkable lustre. The mirrors obtained by brushing the substance over glass are so beautiful and so perfect that it seems as if this property might have useful applications, especially for silvering irregular surfaces. Much care, however, would be necessary in the preparation to obtain a permanent product.

Crystallisation.—On one occasion this substance was obtained in a crystalline form. Some crude red solution had been set aside in a corked vial. Some weeks after, it was noticed that the solution had become decolourised with a crystalline deposit at bottom. The bottle was carefully broken; the deposit, examined by a lens, consisted of short black needles and thin prisms. Evidently the saline matters present had balanced the silver in solution so nearly as not to cause an immediate precipitation, but a very gradual one only. The mother-water was drained off and a few drops of pure water were added. No solution took placed; the crystals were therefore of the material B, the insoluble form. The contact of pure water instantly destroyed the crystallisation, and the substance dried with a bright green metallic lustre. Contact with pure water evidently tends always to bring this form of silver into the colloidal state, sometimes soluble and sometimes not; whilst the contact with certain neutral salts renders it crystalline.

The extraordinary sensitiveness which allotropic silver shows to external influences contrasts strongly with the inertness of normal (probably polymeric) metallic silver. When we place this fact alongside of the well-known sensitiveness of many silver compounds to light, heat, and (as I have elsewhere shown) to mechanical force,* we are led to ask whether silver may not exist in this form in these very sensitive compounds.

To obtain the substance in a pure condition suitable for analysis, it is necessary to choose a precipitant not giving an insoluble product with either citric or sulphuric acid.

* *American Chemical Journal*, Vol. xxxvii., No. 222.

* Production of an image on silver iodide capable of development by simple pressure.

Magnesium sulphate or nickel sulphate answers well; I have generally used the first named. A very dilute solution is made of it, and the red solution of A is to be filtered into it. The precipitate soon subsides. A large quantity of water is to be poured on, and then washing by decantation can be continued to three decantations, after which the substance remains suspended. It can be made to subside by adding a very small quantity of magnesium sulphate; one four-thousandth part (0·25 grm. to one litre) is sufficient. The substance may then be thrown on a filter and washed with pure water.

Analysis.—A specimen dried in vacuo over sulphuric acid gave—

No. 1 .. .. .. 97·17 per cent silver
No. 2 .. .. .. 97·10 „ „

A specimen dried first in vacuo and then at 100° C., lost in the second drying 0·88 per cent water.

So that the substance dried at 100° contained 97·96 per cent of silver. The remaining 2·04 per cent consisted of ferric oxide and citric acid.

C. *Gold-yellow and Copper-coloured Silver.*

It has been long known that golden-yellow specks would occasionally show themselves in silver solutions, but could not be obtained at will, and the quantity thus appearing was infinitesimal. Probably this phenomenon has often led to a supposition that silver might be transmuted into gold.* This yellow product, however, is only an allotropic form of silver, but it has all the colour and brilliancy of gold, a fact which was apparent even in the minute specks hitherto obtained.

By the means presently to be described, silver can be converted wholly into this form. It is a little curious that its permanency seems to depend entirely on details in the mode of formation. I found many ways of obtaining it, but in a few months the specimens preserved changed spontaneously to normal silver. This happened even in well-closed tubes. The normal silver produced in this way is exquisitely beautiful. It has a pure and perfect white colour like the finest frosted jewellers' silver, almost, in fact, exceeding the jewellers' best products. I found, however, one process by which a quite permanent result could be obtained. Specimens made by it in November of 1886 are now, at the end of thirty months, unchanged.

In forming the blue product which I have called A, very concentrated solutions were necessary. C, on the contrary, is best obtained from very dilute ones. The following proportions give good results:—

Two mixtures are to be prepared: No 1 containing 200 c.c. of a ten per cent solution of silver nitrate, 200 c.c. of twenty per cent solution of Rochelle salt, and 800 c.c. of distilled water. No 2 containing 107 c.c. of a thirty per cent solution of ferrous sulphate, 200 of a twenty per cent solution of Rochelle salt, and 800 of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which on the filter has a beautiful bronze appearance. After washing it should be removed whilst in a pasty condition, and spread over watch-glasses or flat basins, and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. The metallic silver formed by reduction with ferrous citrate and ferrous tartrate is in an allotropic condition; with ferrous oxalate this result does not seem to be produced.

Although the gold-coloured silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water: this is essential. It dries into lumps exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. For this substance has in a high degree the property already described in forms A and B—that of drying with the particles in optical contact. When the thick pasty substance is extended over glazed paper, it dries with the splendid lustre of gold leaf, with this essential difference—that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clean glass, beautiful gold-coloured mirrors are obtained; the film seems to be entirely continuous and the mirror is very perfect.

By continued washing the precipitate changes somewhat, so that in drying it takes on a coppery rather than a golden colour, and is rather less lustrous, though still bright and permanent.

Two silver determinations by conversion into chloride made in Nov., 1886, gave—

No. 1 .. .. .. 97·81 per cent silver
No. 2 .. .. .. 97·86 „ „

Recently these experiments have been repeated, and the washing was more successful. Ferric tartrate adheres very obstinately, and after a time washing with water ceases to remove it. Stronger means cannot be employed without affecting the substance itself. These last determinations gave—

No. 1 .. .. .. 98·750 per cent of silver
No. 2 .. .. .. 98·749 „ „

The residue of No. 2 was examined and consisted almost wholly of ferric citrate.

Note.—(By the Editors of the *American Journal of Science*).—The editors have received, from the author of the above paper, samples of the three allotropic forms of silver which he describes, and also strips of glass and paper coated with them. Mr. Lea is to be congratulated on his very important results. The coated strips, including the gold-coloured mirror made with the "gold-silver," answer fully to his description. The mirror is remarkable for its perfection and brilliancy.

THE AMMONIO-COBALTIC MOLYBDATES, TUNGSTATES, AND VANADIATES. SEPARATION OF COBALT AND NICKEL AND OF THE COBALTOUS AND COBALTIC SALTS.

By ADOLPHE CARNOT.

It is known that the ammonio-cobaltic salts differ in several of their characters from the corresponding salts of cobaltous oxide and of nickel. But these characters are not, in general, sufficiently distinct to serve for the recognition and the separation of these salts. This advantage the author finds in certain new salts, the molybdates, tungstates, and vanadiates. For the present he speaks of the molybdates only. If a solution of cobalt is converted into a purpureo-cobaltic salt by oxygenated water in presence of ammonium chloride and ammonia, as formerly indicated (*Comptes Rendus*, April 8th. 1889), and if ammonium molybdate is added, there ensues no turbidity and no change of colour. But if the liquid is neutralised and acidified with acetic acid there is at once produced a bulky precipitate of a fine peach-blossom

* I have a little volume published in Paris in 1857 by a chemist named Tiffereau who was firmly convinced that in many reactions minute portions of silver are converted into gold, especially with the aid of powerful sunlight. In Mexico, he affirmed, he had artificially produced several grms. of gold, a portion of which he presented to the French Academy with one of his papers. To his great disappointment he did not succeed in repeating these experiments in Paris with more than an infinitesimal result. All gold in his opinion had been originally silver, and this belief, he affirms, is universal among Mexican miners. The book has for title "Les Métaux sont des Corps composés."

colour. This precipitate, which is almost absolutely insoluble, collected on a filter, washed, and dried at 100°, remains of a rose colour. If heated more strongly it takes a violet tint and passes through blackish green and greenish yellow colours, changes which correspond to successive eliminations of water, of ammonia, and of oxygen. The matter becomes a cobaltous molybdate and has a lilac colour when cold. If the temperature of dull redness is exceeded it undergoes a partial dissociation with formation of black cobalt oxide and of molybdic anhydride in small crystals.

The analysis of the rose-coloured salt, dried at 100°, was excecuted by decomposing with potassa-lye, collecting the ammonia in a standard solution of sulphuric acid, isolating the insoluble cobalt peroxide, and determining the cobalt after reduction by hydrogen. Lastly, the alkaline molybdate was converted into sulphomolybdate and the molybdenum weighed as sulphide. The water was calculated as difference. The author gives the composition of the dried salt as $Co_2O_3,5NH_3,7MoO_3 + 3HO$, and when calcined, $2CoO.7MoO_3$.

The salts of cobaltous oxide and the nickel salts give no precipitate with ammonium molybdate either in an acetic or an ammoniacal precipitate. A crystalline deposit of the double ammonium and cobalt (or nickel) may indeed be formed, but it is only produced slowly and in liquids which are nearly neutral and very concentrated, conditions easily avoided.

The reaction just indicated gives the means, not previously possessed, to recognise the ammonio-cobaltic salts, and even to determine them in presence of cobaltous salts. It is merely necessary to acidify the solution with acetic acid and to add the molybdic reagent. The precipitate will contain all the ammonio-cobaltic salt and the liquid all the cobaltous salt. We may in this manner solve various questions, and even follow the progress of the peroxidation of cobalt in ammoniacal solutions left to themselves or traversed by a current of air. The same method enables us to separate cobalt and nickel, as the latter is not peroxidised by hydrogen peroxide in an ammoniacal solution. The following are the necessary details of the operation:—

The two metals being in a hydrochloric or nitric solution we add ammonium chloride and ammonia in excess and then a little oxygenated water. After a few minutes the mixture is gently heated to a boil. When the effervescence due to the escape of oxygen has completely ceased it is let cool. Cold water is added if the colour of the liquid shows that it is too concentrated. We neutralise with acetic acid and add further 3 to 5 c.c. of this acid to 100 c.c. of the liquid and then add a solution of ammonium molybdate until no further turbidity is occasioned. It is let settle, decanted, and the precipitate is received upon a filter and washed with water and a few drops of ammonium chloride. After desiccation it can be easily and almost completely separated from the paper, which is burnt separately. Lastly, the precipitate is ignited, but without exceeding dull redness. It is then let cool and weighed. The weight is multiplied by the coefficient 0·1332 to find the weight of the cobaltous oxide and by 0·1048 to have that of the metal. The weight of the ignited molybdate is therefore approximately ten times that of the cobalt.

The rose-coloured precipitate of ammonio-cobalt molybdate is very bulky and very characteristic. The method furnishes consequently a highly sensitive method of qualitative detection, showing traces of cobalt in the commercial salts of nickel. It is applicable also in presence of copper and zinc.

The separation of the metals, as well as the determination of the cobalt, is very exact, especially for small quantities, from some milligrms. up to at most 1 decigrm. The better to remove foreign salts, it is well to re-dissolve the precipitate while still moist in ammonia-water, and to re-precipitate by rendering the liquid slightly acetic and adding a little ammonium molybdate.

To determine the nickel in the filtrate a sufficient quantity of caustic potassa is added, and the liquid is heated to ebullition, so as to expel the ammonia and entirely precipitate the nickel hydroxide. It is received on a filter, re-dissolved in hydrochloric or nitric acid, and precipitated afresh, using potassa and bromine. The sesquioxide obtained retains not a trace of molybdate, and may be determined either by means of a standard solution or by reducing in hydrogen and weighing the metallic nickel.—*Comptes Rendus* (vol. cix., p. 109).

A CONVENIENT FORM OF PIPETTE FOR MEASURING OUT BEET, CANE, AND SORGHUM JUICES FOR POLARISATION.

By C. A. CRAMPTON.

IN "Bull. No. 15, Chem. Div. U.S. Dept. Agr.,"* I have described the method of procedure followed by the analysts at the Stations of this Department in the analysis of juices. For polarisation it has been the custom to measure out a sample of juice, as it would require too much time to weigh, and for this purpose it has been the custom to measure out 50 c.c. with a pipette,

making subsequent correction of the polarisation for the specific gravity of the juice. When the polariscope used is one that has the factor 26·048, that is, requires 26·048 grms. of pure sugar, dissolved and made up to 100 c.c. of water, to read 100 on the scale, it will be seen that 50 c.c. of juice gives a weight in grms. very nearly twice the normal amount to be taken for the instrument, or 52·096. Last year I had some pipettes made, which were graduated in the stem from 48 to 54 c.c., with sub-divisions of 0·5 c.c., to be used in measuring out directly the correct amount of juices of different densities, to give double their polarisation; the number of c.c. to be used for each

* Also in CHEM. NEWS, lv., 207.

density to be ascertained from a table. These pipettes were used during the present sugar campaign in Louisiana by Mr. G. L. Spencer, at Magnolia Station, who found them very convenient. He has calculated a table to be used in connection with them.

I have had made recently a modification of this pipette, which does away with the necessity of a table, and which is illustrated in the accompanying cut. It is graduated from 48·1 to 51·1 c.c., the sub-divisions being in tenths of a c.c., but the divisions are marked instead with degrees Brix, having a range from 5° to 20° each, 0·1 c.c. division corresponding to 0·5° Brix. That is, after the degree Brix of a juice has been ascertained, the pipette, when filled up to the corresponding mark on the stem, will deliver 52·096 grms. of the juice (within a few m.grms., which is as close as it is possible to weigh it out). So it is necessary to divide the polarisation by two, or to read the solution in a 400 m.m. tube, to give directly the per cent of sucrose in the juice.

The calculation for the graduations is taken from Stammer's table for specific gravities and the corresponding degrees Brix. For commercial work these pipettes will weigh out the juice with sufficient accuracy, and I think they will prove convenient for rapid work, and save considerable time in the calculation of results.—*Journal of Analytical Chemistry*, Vol. iii., Part 1.

ANALYSES OF SOME CISTERN-DEPOSITS.

By ALFRED S. CHAPMAN, F.C.S.

A short time ago Professor Graham, of University College, handed me three mineral deposits, taken from a copper cistern in which water had been softened by Clark's process, and suggested that I should submit them to analysis. The results are, I venture to think, of sufficient interest to warrant their publication. These three substances I shall refer to, for sake of simplicity, as A, B, and C.

Deposit A.—This was a very hard grey stone; a broken surface having a slightly rough and crystalline appearance. Its weight was about 6 grms.

Deposit B.—A hard stone of a light buff colour. It was of a very compact nature, a broken surface appearing perfectly smooth. It weighed about 4·5 grms.

Deposit C.—A rough green-coloured deposit, somewhat resembling terre-verte in appearance. It was very much softer than either A or B, and weighed only 0·6 grm.

The following are the results of the analysis of deposit A:—

Lime	52·19
Oxide of iron	8·40
Silica	19·68
Carbonic acid	5·70
Water of combination ..	13·60
Trace $MgSO_4$ &c.	0·43
	100·00

After converting the carbonic acid into its equivalent of carbonate of lime (= 12·95 per cent) and then combining the silica with as much lime as is required to form the neutral silicate, it will be found that there is still 26·58 per cent lime left uncombined, which I have every reason to believe exists in combination with the calcic silicate and water, forming a hydrated basic silicate. After converting the 5·7 per cent carbonic acid into 12·95 per cent carbonate of lime there is 44·94 per cent lime left. The ratio of this number (the amount of lime existing as a basic silicate) to the percentage of silica (19·68) is as 2·20 : 1.

I shall refer to this ratio in connection with the next analysis:—

Results of Analysis of Deposit B.

Lime	53·20
Oxide of iron	1·80
Magnesia	0·32
Carbonic acid	34·37
Silica	4·30
Sulphuric acid	0·71
Water of combination, moisture, &c., by difference	5·30
	100·00

In this case, after combining the lime with the silica (to form the neutral silicate) and with the carbonic acid, there is 5·45 per cent uncombined lime. If, as in the last case, the 34·37 per cent carbonic acid be converted into 78·11 per cent carbonate of lime there remains 9·46 per cent lime. The ratio of this number, which is the amount of lime existing probably as a hydrated basic silicate, to the percentage of silica (4·30) is as 2·28 : 1. Hence it appears permissible to conclude that in each of these two deposits there exists a basic silicate of lime of the same composition. The mean of these two ratios (2·24 : 1) is very nearly that which would occur in the compound $2CaSiO_3.3CaO$.

There was not sufficient of B for a direct determination of the water of combination, but if, in the analysis of A, the ferric oxide be converted into ferric hydrate, the remaining water and the percentage of lime and silica are nearly those numbers which would be required for the compound $2CaSiO_3.3CaO+4H_2O$.

Examination of Deposit C.

This substance, which I thought at first might be a basic carbonate of copper, I found on examination to contain, in addition to copper and carbonic acid, considerable quantities of silica and arsenic. The quantity at my disposal (0·6 grm.) was too small for a complete quantitative analysis, but the following are some results obtained:—

Silica	19·8 per cent.
Carbonic acid .	1·8 ,,

A determination of the arsenic gave rather more than 5 per cent, but this number is only approximate.

University College, July 18, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

(Concluded from p. 49).

67. "*Note on the Oxidation of Paradiamines.*" By R. Meldola, F.R.S., and R. E. Evans.

It is well known that quinones are formed by the oxidation of benzenoid paradiamines, and it is generally believed that the amido-groups are split off in the form of ammonia, but it does not appear that any quantitative determination of the amount of ammonia produced has been made. The authors have, therefore, made a series of experiments with paraphenylenediamine prepared by the reduction of paranitraniline, using the base in the form of the sulphate, this salt being easily purified by crystallisation. After several preliminary trials, the most convenient mode of procedure was found to be as follows:—The calculated quantity of potassium dichromate was dissolved in water, and the solution of the diamine sulphate poured in; the mixture was allowed to stand for two days at the ordinary

temperature, and then filtered to remove the quinone and its associated impurities. The filtrate was made distinctly acid with dilute sulphuric acid, and evaporated on a water-bath to a small bulk, then transferred to a flask and made alkaline with caustic soda. The ammonia was driven off by a current of steam, and received in dilute chlorhydric acid. The distillate was evaporated to dryness in a weighed dish, and the dry residue weighed as ammonium chloride. 5 grms. of paraphenylenediamine sulphate treated in this way gave 2·38 grms. of ammonium chloride. The quantity required by theory is 2·6. The ammonium chloride was tested qualitatively, and found to be free from impurities.

68. "*Monobenzyl-derivatives of the Phenylenediamines.*" By R. Meldola, F.R.S., and J. H. Coste.

Monobenzylparaphenylenediamine was prepared by reducing monobenzylparanitraniline (Meldola and Salmon, *Trans.*, 1888, 774) with tin and chlorhydric acid, and removing the tin as sulphide. The dihydrochloride, $C_6H_4{\cdot}NH_2{\cdot}NH{\cdot}C_7H_7{\cdot}2HCl$, forms lustrous white scales readily soluble in water, less soluble in chlorhydric acid, and almost insoluble in alcohol. Ferric chloride gives a green colouration when added to the aqueous solution, this colour soon changing into red. The diacetyl-derivative, $C_6H_4{\cdot}NHAc{\cdot}NAc{\cdot}C_7H_7$, forms colourless hexagonal prisms melting at 116·5—117°. The dibenzoyl-derivative forms white needles melting at 124°. One mol. prop. of the benzyldiamine oxidised in the presence of one of benzylaniline gives the dibenzylindamine, $C_7H_7{\cdot}HN{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}N{\cdot}C_7H_7$. This compound, which is of an intense greenish blue colour with a coppery lustre, rapidly undergoes spontaneous decomposition, and becomes converted into what is apparently a mixture of benzylbenzylidene- and dibenzylidene-diamidodiphenylamine,—

$$NH<\begin{matrix}C_6H_4{\cdot}N{:}CH{:}C_6H_5\\C_6H_4{\cdot}NH{\cdot}CH_2C_6H_5\end{matrix} \text{ and } NH<\begin{matrix}C_6H_4{\cdot}N{:}CH{\cdot}C_6H_5\\C_6H_4{\cdot}N{:}CH{\cdot}C_6H_5\end{matrix}.$$

One molecule of the benzyldiamine oxidised in the presence of two molecules of benzylaniline at the temperature of boiling water gives an azine or benzylated saffranine, which is of interest as being produced, in contradiction to the generally received view, from one molecule of a diamine and two molecules of a *secondary* monamine. The free amido-group of the benzyldiamine can be diazotised by the action of nitrous acid, and the diazo-salts combine with phenols in the usual way to produce azo-compounds. Of the latter, the azo-derivatives of α- and β-naphthol have been prepared. The free base, benzylparaphenylenediamine, has been isolated, and forms reddish moss-like crystalline aggregations; the melting-point is 30°; the base reddens by oxidation on exposure to the air. Monobenzylmetaphenylenediamine was prepared in a similar manner to the above by reducing benzylmetanitraniline. The free base is oily at the ordinary temperature; the dihydrochloride forms dense laminated rhombohedra of an ochreous colour. The aqueous solution of the latter salt gives a red colour passing into orange-brown on the addition of ferric chloride. On heating the solution with ferric chloride or other oxidising agent a white insoluble product of oxidation settles out. The diacetyl-derivative of the benzylmetadiamine forms an uncrystallisable resin; the dibenzoyl-derivative forms rhomboidal plates melting at 178°. By oxidising equi-molecular proportions of the benzylmeta- and benzylpara-diamines, a deep indigo-blue indamine i precipitated. This colouring matter is fairly stable in th cold, but passes into an azine on heating.

69. "*Note on a Yellow Pigment in Butterflies.* By F. Gowland Hopkins.

For the most part the colour effects on the wings of lepidopterous insects are probably due to purely physical causes, and not to the presence of any definite pigment. But in some cases pigments are undoubtedly present. These are for the most part very difficult to isolate; but an exception to the rule occurs in the case of a certain yellow pigment which is found in its purest form in the common English brimstone butterfly. The pigment may also be detected in the wings of a very large number of day-flying lepidoptera. It may be obtained from the wings by simple treatment with hot water, in which it is freely soluble, and it may be identified by its yielding a marked murexide reaction when evaporated with nitric acid and afterwards treated with ammonia or potash.

The wings should be first treated with hot alcohol and ether, in which the pigment is insoluble, then boiled up with water, and the yellow aqueous solution filtered while hot. If the aqueous solution be now concentrated to a small bulk and allowed to cool, the substance separates out as a yellow amorphous precipitate. It may be purified by dissolution in a fresh quantity of hot water, whence it again separates on cooling. Otherwise it may be removed from the wing by the action of dilute alkalies in the cold, and afterwards precipitated by the addition of acetic acid. The common brimstone butterfly yields somewhat less than a m.grm. of pigment from each insect; larger foreign species, such as those belonging to the genus *Callidryas*, may yield as much as 4—5 m.grms.

The pigment is an amorphous powder insoluble in alcohol, ether, chloroform, and all the more common organic solvents. It is very sparingly soluble in cold, but freely so in hot water.

Its aqueous solutions have a fine blue fluorescence and are strongly acid to litmus. The substance is freely soluble in alkalies, yielding with them solutions darker in colour than is its aqueous solutions; from these it is precipitated when neutralised with acetic acid.

It thus agrees closely in its physical properties with *mycomelic acid*, a yellow derivative of uric acid, though its yellow colour is more decided than is that of the latter substance. Mycomelic acid does not, however, yield a murexide reaction; while the pigment, as stated above, does so in a very marked manner. If it be boiled for some time with chlorhydric acid it is decomposed, and crystals of uric acid separate out, coloured much in the same manner as when obtained from acidified urine; on prolonged boiling with the dilute acid, urea is formed together with other crystalline substances not yet determined. There can be no doubt that the pigment is a derivative of uric acid, probably allied to mycomelic acid. It appears not improbable to the author that it may indeed be a condensation product of the two acids uric and mycomelic, and progress towards its synthesis has been made in this direction. If it be supposed that the two acids unite with elimination of two mols. of water to form a new dibasic acid, the acid would yield a silver compound containing 44·44 per cent of silver. The pigment under discussion gives a perfectly definite silver compound, the amount of silver found in three analyses being 44·61, 44·66, and 44·42 per cent.

The author hopes shortly to obtain a sufficiency of the substance for accurate ultimate analysis.

70. "*Zinc Dextrosate.*" By A. C. Chapman.

This compound is prepared by dissolving zinc hydrate in the smallest possible quantity of ammonia solution, and adding the liquid to a solution of dextrose in 90 per cent alcohol; its composition is represented by the formula $C_6H_{12}O_6{\cdot}2ZnO{\cdot}3H_2O$.

71. "*β-Bromonaphthalenesulphonic Acid.*" By R. W. Sindall.

Whereas the two isomeric acids obtained on sulphonating β-chloronaphthalene by means of SO_3HCl—no heat being applied except in distilling off the carbon disulphide used as solvent of the chloronaphthalene—have been shown to correspond respectively to the so-called Badische and Brönner modifications of beta-naphthylaminesulphonic acid, the 2 : 1′ being the chief, and the 2 : 3′ the subsidiary product, the experiments made by Mr. W. Houlding (*Chem. Soc. Proc.*, 1889, 74) have shown that in the case of β-iodonaphthalene the result is different, inasmuch as the β-iodo-acid prepared

from the Brönner β-amido-acid is not identical with either of the two β-iodo acids formed by direct sulphonation of β-iodonaphthalene. Mr. Houlding has shown that the bromo acid prepared from the Brönner β-amido acid is identical with the minor product of sulphonation of β-bromonaphthalene; to determine the nature of the major product of sulphonation, the author has prepared the isomeric acids from the three isomerides of Brönner's β-amido acid.

2 : 1′ *Bromonaphthalene-α-sulphonic Acid.*—Although this acid has been prepared by Forsling (*Ber.*, 1889, 619), the account which he gives is insufficient for the purposes of comparison. The author finds, as was to be expected, that the bromo-acid prepared by the Griess-Sandmeyer process from the Badische β-amido-acid is identical with the major product of sulphonation of β-bromonaphthalene (cf. *Chem. Soc. Proc.*, 1887, 23). The sulphochloride melts at 147°; the sulphobromide, as stated by Forsling, at 151°; the sulphonamide melts at about 209°.

2 : 4′ *β-Bromonaphthalene-α-sulphonic Acid.*—This acid was prepared from the Dahl β-amido-acid. Its sulphochloride crystallises well from light petroleum in aggregates of small prisms melting at 77°; the sulphonamide melts at about 217°.

2 : 2′ *β-Bromonaphthalene-β-sulphonic Acid.*—Mr. Houlding had prepared this acid from the δ- (Bayer and Duisberg) amido-acid; the author has repeated the experiments. The sulphochloride crystallises from benzene in massive, oblique prisms melting at 100°; the sulphonamide melts at about 218°.

On distilling the sulphochlorides of the four β-bromo-acids with phosphorus pentachloride, the product obtained chiefly consists of the corresponding *dichloronaphthalene*, both the bromine atom and the SO_2Cl group becoming displaced by chlorine. In Mr. Houlding's paper (*loc. cit.*) the melting point 137° is wrongly assigned to 2 : 3′ chloro-bromonaphthalene.

72. "*Isomeric Change in the Naphthalene Series.* No. 5. *β-Iodonaphthalenesulphonic Acids.*" By Henry E. Armstrong and W. P. Wynne.

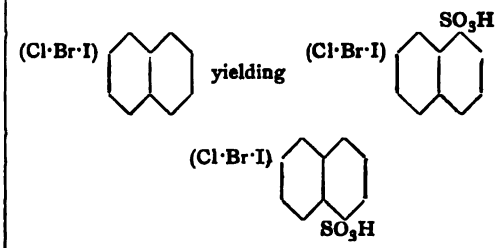
The authors describe the results obtained on carrying out the experiments referred to at the close of a recent communication by Mr. W. Houlding (*Chem. Soc. Proc.*, 1889, 74, *cf. infra*).

2 : 2′ *β-Iodonaphthalene-β-sulphonic Acid.*—This acid was prepared by Mr. Houlding from betanaphthylamine-δ-sulphonic acid. Its sulphochloride crystallises from benzene in aggregates of small prisms melting at 100°; its sulphonamide melts at 210°. It is not identical with either of the acids produced on sulphonating β-iodo-naphthalene.

2 : 1′ *β-Iodonaphthalene-α-sulphonic Acid.*—The authors have prepared this acid from the Badische modification of betanaphthylaminesulphonic acid, and find that, as was to be supposed, it is identical with the major product of sulphonation of β-iodonaphthalene by SO_3HCl. It is to be noted, however, that the sulphochloride melts at 164—165°, and not at 174° as by mistake has been previously stated (*B.A. Report*, 1887, 234), the sulphonamide melts at about 240°.

2 : 4′ *β-Iodonaphthalene-α-sulphonic Acid.*—On preparing this acid from the Dahl modification of betanaphthylaminesulphonic acid, it was found to be identical with the acid obtained as minor product on sulphonating β-iodonaphthalene by means of SO_3HCl. The sulphonchloride melts at 92·5°; the sulphonamide at about 213°.

Although, therefore, the major product of sulphonation in the case of β-chloro-, bromo-, and iodonaphthalene is the 2 : 1′ *alpha*-sulphonic acid, the minor product is different: β-iodonaphthalene yielding a second *alpha*-sulphonic acid, whereas β-chloro- and bromo-naphthalene each give the 2 : 3′ *beta*-sulphonic acid; and it should also be stated that a smaller proportion of the acid which is the subsidiary product is obtained both from chloro- and from bromo- than from iodonaphthalene. Two explanations of the dissimilarity are possible, viz.: either that there is an initial difference of behaviour or that there is no initial difference, but that isomeric change takes place in the case of the chloro- and bromo-, and not in the case of the iodo-compound. The latter appears the more probable. It may be supposed that initially on sulphonation two isomeric acids are formed—



and that in the case of chloro- and bromo-naphthalene one of these—the 2 : 4′ acid—*at once spontaneously* undergoes isomeric change into the 2 : 3′ isomeride, no such alteration, however, occurring in the case of the iodo-acid. There is much independent evidence that such a change may well occur: thus on sulphonating 1 : 4 dichloronaphthalene a heteronucleal dichloro*beta*-sulphonic acid is obtained as sole product; but there is every reason to believe that the actual product of sulphonation is an *alpha*-acid, and if this be the case isomeric change must take place spontaneously, and with exceptional facility and completeness. 1 : 3 Dichloronaphthalene yields only an alpha-sulphonic acid. 1 : 2 Dichloronaphthalene, however, affords a mixture of about two-thirds 1 : 2 : 4′ *alpha*-sulphonic acid with one-third of the isomeric 1 : 2 : 3′ *beta*-sulphonic acid (cf. *Chem. Soc. Proc.*, 1889, 52); this latter the authors believe to be a product of spontaneous isomeric change occurring at the moment of sulphonation, and that this is the case is placed almost beyond question by the observation that if the mixed product of sulphonation be heated at 150—160° during ten hours, the alpha-sulphonic acid almost entirely disappears, the beta-acid taking its place.

It has previously been shown that 2 : 1′ β-chloro-naphthalene-α-sulphonic acid is converted into the 2 : 3′ acid by heating it at about 150° (cf. *Chem. Soc. Proc.*, 1887, 145). The 2 : 1′ iodo-acid should therefore be convertible into the 2 : 3′ isomeride, and this is found actually to be the case. The product obtained on sulphonating β-iodonaphthalene and then heating the resulting mixture of alpha-acids at 150° during about five hours, in fact, consists almost entirely of the 2 : 3′ iodo-acid identical with that prepared from the Brönner betanaphthylaminesulphonic acid, showing clearly that not only the 2 : 1′ but also the 2 : 4′ acid passes by isomeric change into the symmetric ββ 2 : 3′ acid.

73. "*The Formation of Sulphones on Sulphonating Naphthalene Derivatives by means of Chlorosulphonic Acid.*" By W. M. Heller.

When naphthalene and its monohaloid derivatives are sulphonated by means of SO_3HCl, a varying but always small proportion of sulphochloride is usually obtained, but apparently this is a secondary product, and results from the action of the SO_3HCl on the sulphonic acid which is first formed.

On sulphonating 1 : 4 chlorobromonaphthalene, dissolved in carbon bisulphide, by SO_3HCl, using equimolecular proportions of the interagents, the author has found that the whole of the naphthalene compound is acted on, but that only a relatively small amount of sulphonic acid is obtained, the chief product being the sulphone,—

$$(C_{10}H_5ClBr)_2SO_2,$$

no sulphochloride being formed. The corresponding β-dichloro- and dibromo-naphthalene behave similarly. The melting points of the sulphones thus obtained, and

of the sulphochlorides prepared from the corresponding sulphonic acids, are as follows :—

$\beta Cl_2 \cdot SO_2Cl$	133°	Cl_2 sulphone about	216°
$\beta ClBr \cdot SO_2Cl$	—	ClBr ,,	224°
$\beta Br_2 \cdot SO_2Cl$	119°	Br_2 ,,	236°

The sulphones are almost insoluble in benzene, but may be crystallised from xylene.

On sulphonating γ-dichloronaphthalene (m. p. 107°) by SO_3HCl, a small amount of a compound melting at 265° is obtained, which probably is also a sulphone. The corresponding chlorobromonaphthalene, however, appears to yield only sulpho-acid ; the chloride of this acid melts at about 155°.

74. "*Note on the Hydration of Cyanides.*" By Henry E. Armstrong.

Experiments made at the author's request by Mr. Houlding with the object of comparing the behaviour towards sulphonating agents of β-cyanonaphthalene with that of α-cyanonaphthalene have shown that, unlike the latter, the β-compound is not susceptible of sulphonation ; if, however, it be dissolved in fuming sulphuric acid and the solution be cautiously poured into water, it is completely converted into β-naphthoeamide, $C_{10}H_7 \cdot CO \cdot NH_2$.

In like manner, Mr. Percival has found that on adding trichloracetonitril, $CCl_3 \cdot CN$, to sulphuric anhydride a liquid is obtained which gradually solidifies to a mass of crystals of a compound of the nitril with the anhydride; on adding this compound to water, it undergoes immediate and complete conversion into trichloracetamide.

These two cases appear to afford striking evidence in favour of the view that hydrating and hydrolytic agents act by forming compounds directly attackable by water; they serve, in fact, to support the integration rather than the dissociation hypothesis of chemical change. It is not improbable that the non-conversion of pentamethylbenzonitril into the corresponding acid to which Hofmann has called attention, and the recent similar observation made in Victor Meyer's laboratory (*Annalen*, 250, 147) are to be explained as consequences of the incapability of the cyanide in question to form compounds with the hydrating agents used; and that perhaps sulphuric anhydride will be found available in these cases also.

75. "*The Existence of Salicylic Acid in Certain Genera of the Liliaceæ.*" By A. B. Griffiths.

The author states that he has isolated salicylic acid from the leaves, stems, &c., of *Tulipa*, *Yucca*, and *Hyacinthus* in the following manner :—

The leaves, stems, &c., cut up into small pieces, were digested with ether and the solution distilled. The residue was treated with distilled water and the solution filtered ; the filtrate was then neutralised with potassium carbonate, evaporated, and finally distilled with pure chlorhydric acid. The aqueous distillate yielded on evaporation colourless, prismatic crystals, which were found to be soluble in ether, alcohol, and boiling water, but sparingly soluble in cold water.

A solution of the crystals gave with ferric chloride a deep violet colour. A series of combustion analyses of these crystals were carefully performed, which he states gave the composition of salicylic acid. The crystals were found to melt at 131° C., and on distilling them with lime, phenol and carbon dioxide were readily produced.

The author states that he has estimated the percentage of the acid in various parts of the plants with the following results :—

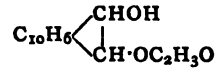
	Tulipa.	Yucca.	Hyacinthus.
Leaves	0·0989	0·1410	0·1103
Peduncles ..	0·0812	—	0·0788
Stems	—	0·1065	—
Bulbs	0·0542	—	0·0483
Flowers ..	trace	—	trace

76. "*On the Oxidation Products of Acenaphthene.*" By T. Ewan, B.Sc., and J. B. Cohen, Ph.D., Owens College.

These experiments were undertaken with the view of preparing the products of oxidation intermediate between acenaphthene and naphthalic acid.

By the action of lead oxide and water upon dibromacenaphthene bromide, a yellow crystalline compound melting at 126—129° was obtained, which has the formula $C_{12}H_4O_2Br_2$.

Acenaphthylene glycol monoacetate,—



is obtained by converting acenaphthylene dibromide into the acetate, and decomposing the product with potash ; m.p. 122—122·5°.

Acenaphthylene glycol diacetate,—

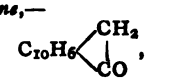
$$C_{10}H_6(CH \cdot OC_2H_3O)_2,$$

is obtained by boiling the monacetate with excess of acetic anhydride ; m.p. 130°.

Acenaphthylene glycol is prepared by decomposing the monoacetate with boiling alcoholic potash. It crystallises in colourless needles melting at 204—205°.

Acenaphthylene glycol monobenzoate is obtained by acting upon the dibromide with silver benzoate. It crystallises in plates melting at 189—190°.

Acenaphthene ketone,—



is prepared from the glycol by the action of sodium alcoholate. It crystallises in pale yellow needles melting at 119—119·5°.

The alkyl ethers of the glycol cannot be obtained by any of the usual reactions. If acenaphthylene bromide be acted on by sodium ethylate in alcoholic solution acenaphthene is formed, and if the bromide be treated with anhydrous sodium ethylate in benzene solution acenaphthylene is produced.

Tetrabromacenaphthene, $C_{12}H_6Br_4$, is formed by the action of bromine dissolved in carbon bisulphide upon acenaphthylene bromide ; m. p. 161—162°.

Tribromacenaphthene, $C_{22}H_7Br_3$, is prepared in a similar manner ; m. p. 88—90°.

Chromium oxychloride reacts with acenaphthene in CS_2 solution, and forms a well-defined addition compound, but the diketone could not be obtained. The authors have prepared crystalline compounds by distilling the barium salt of naphthalic acid with the lime salt of the fatty acids, which are probably the aldehyd and ketone-derivatives of naphthalic acid. Acenaphthene reacts with the acid chlorides in presence of aluminium chloride, forming ketones.

A crystalline compound has also been obtained by the action of PCl_5 upon naphthalimide. The investigation of these compounds will form the subject of a subsequent communication.

77. "*Schutzenberger's Process for the Estimation of the Oxygen Dissolved in Water.*" By Sir Henry E. Roscoe, F.R.S., D.C.L., LL.D., and Joseph Lunt, B.Sc., Associate of the Owens College.

The authors find that a series of estimations made on the same sample of London tap water give results which differ 35 per cent from the mean value, and that the time taken in titrating has a great influence, much higher results being obtained if titration be quickly than if it be slowly performed. The disturbing influence has been traced to the fact that when aërated water is introduced into an atmosphere of hydrogen, as in the usual process, it immediately begins to lose oxygen by diffusion, a fact hitherto overlooked. The result of an oxygen estimation thus depends on the degree of exposure to hydrogen during titration, and results between 0·53 and 7·56 were obtained with the same water by varying the exposure.

Under favourable circumstances 20 per cent of the dissolved oxygen diffuses, whilst in the usual form

of the apparatus 50 per cent of the oxygen diffuses during the estimation. An exposure of three minutes is sufficient to permit all the dissolved oxygen to escape. This explains the return of the blue colour during an estimation carried out in the usual manner, the *diffused* oxygen becoming re-absorbed by the reduced indigocarmine. No return of the blue colour takes place on reducing indigocarmine when free oxygen is absent, and the action has been proved to be due to the supernatant gas, and not to any action occurring within the liquid, as Schützenberger supposed.

Diffusion also explains the observation made by Schützenberger that twice the amount of oxygen is found when a large amount of reduced indigocarmine is present; in that case the dissolved oxygen is at once acted on, and so cannot diffuse.

Ramsay and Williams, who have investigated the process, do not obtain twice the amount, but only an increase in the ratio of 3 : 5. Diffusion also explains this observation, a smaller vessel having been used in their experiments a larger proportion of the oxygen was found in the usual process, in other words, three-fifths of the whole.

The method adopted to eliminate this error, due to diffusion, is to run the aërated water beneath the surface of a liquid containing a measured excess of hyposulphite, and a little reduced indigocarmine as an indicator. In this way the dissolved oxygen is immediately acted on by the hyposulphite and its diffusion prevented. For the standardisation of the hyposulpbite the two methods hitherto used were found inaccurate. The copper method being fundamentally wrong owing to a secondary action which occurs between sulphite and dissolved oxygen. The aërated distilled water method, hitherto used with Bunsen's absorption coefficients, the authors show to be inaccurate, giving the values obtained by them, which agree closely with observations made by Dittmar.

The new method of carrying out the process and the corrected values for the oxygen dissolved by distilled water give results for which perfect accuracy cannot be guaranteed, but which are not far removed from the truth, and certainly valuable. The reaction is much disturbed by the presence of free acid or alkali.

78. "*Isomeric Change in the Phenol Series*" (Third Notice). By Arthur R. Ling.

The author finds that chlorine under a variety of conditions does not affect the conversion of ortho- into para-nitrophenol-derivatives; bromine alone appears to have this property.

He corrects a previous statement that orthochloroparabromorthophenol is converted by the action of bromine into parachlororthobromorthonitrophenol.

On treatment with nitric acid parachlororthobromorthonitrophenol yields parachlorodiorthonitrophenol, whereas parabromorthochlorothonitrophenol is converted into orthochloroparadinitrophenol—the bromine and not the chlorine atom being always displaced.

Orthochloroparabrom*orthonitro*phenol appears to undergo isomeric change when treated with bromine, yielding the isomeric orthochlororthobrom*paranitro*phenol together with orthochlordinitrophenol and chlorotribromoquinone.

NOTICES OF BOOKS.

Alkali, &c., Works Regulation Act, 1881. *Twenty-fifth Annual Report on Alkali, &c., Works by the Chief Inspector. Proceedings during the Year* 1888. Presented to the Local Government Board and to the Secretary of State for Scotland. London: Her Majesty's Stationery Office.

This Report, as usual, is replete with interesting matter, both as bearing on public health and on the industrial position of the country.

The total number of works in the United Kingdom, registered under the Act, was at the close of 1888 1057, a decrease of 9 as compared with 1887. The falling off has occurred chiefly in Scotland. In the number of processes under inspection there has been no great change. The larger works seem to be, as a whole, increasing in size, whilst the smaller ones tend to close their operations.

The visits of inspection, in case of works in full activity, are made about once a month, but the intervals are quite irregular. No notice is given, and the escaping gases may be sampled for analysis even in the night.

It is satisfactory to find that in all the districts, save one, the average amount of acid gases escaping falls below one-half of the limit fixed by the Act. In all cases there appears to be a slight, but constantly progressive, improvement.

Prosecution has been found necessary in eight cases, in six of which the offence was neglect of registration.

It is pleasant to find that the inspectors are now regarded by manufacturers by no means in the light of enemies. An eminent manufacturer, Mr. Chance, of Oldbury, said, in a discourse delivered before the Philosophical Society of Birmingham:—"In my opinion Government inspection has not only led to material improvements in the general management of chemical works, but it has been in reality a distinct benefit to, rather than a tax upon, the owners of such works."

As regards the statistics of the alkali trade, an improvement is perceptible as compared with 1887. The quantity of alkali produced by the ammonia process is equivalent to 212,181 tons of salt decomposed, as against 158,636 tons in 1887. Yet, in the face of this advance, the decline in the Leblanc process has ceased, and been succeeded by a revival. The salt consumed in this process was in 1886, 584,323 tons, and in 1887 it had fallen to 577,381 tons; but in 1888 it rose to 590,312 tons. The ammonia-soda makers have not yet succeeded in producing bleaching-powder by their process, and the Leblanc makers, on the other hand, thanks to the inventive skill of Mr. A. M. Chance, of Oldbury, are now able to recover 90 per cent of the sulphur, till lately wasted,—expensively and annoyingly wasted,—in the form of tank waste. The recovered sulphur fetches the highest price of any in the market, and will, it is hoped, compete seriously with Sicilian sulphur.

The processes of Messrs. Parnell and Simpson, and of Mr. F. Gossage, are likewise very promising. The former will recover the sulphur from the waste, whilst the latter seems likely to prevent its future formation.

The maintenance of the Leblanc process is of no small national importance, since, though soda is being abundantly and profitably made in Britain by the rival method, yet we have about £3,000,000 of capital sunk in plant which would be of little, if any, use for other purposes.

The quantity of ammonia produced in the country in the form of sulphate is steadily increasing, and has now reached 122,785 tons, as against 113,896 tons in 1887. Its value is upwards of £1,400,000 yearly.

The subject of black coal-smoke, though not in itself falling within the provisions of the Act, has been brought under the notice of the Inspector in consequence of a report which had gained credence in Manchester and elsewhere that black smoke is a guarantee for the absence of the deadly carbon monoxide. A chemist would at once perceive the absurdity of this view, which was actually brought forward in a court of law as a plea in mitigation of the penalty incurred for the production of black smoke. For the benefit of the non-chemical public the Inspector had the combustion gases from a number of chimneys analysed. Carbon monoxide was not often found, but when it occurred it was always in company with black smoke. "In every case where the black smoke is absent this gas is absent also."

There are hopes that the "thermo-motor" devised by

Mr. Hargreaves may cut away altogether the causes of the smoke nuisance. A 40 horse-power engine on this principle is already in successful operation.

Mr. Mond's system of using gaseous fuel is also of high promise, since it not merely gives a smokeless sootless fire, but saves the ammonia which in other systems is wasted.

In the separate report addressed to the Secretary of State for Scotland there is reference in speaking of tank-waste to an abomination which, I fear, is increasing. At one of the Scottish alkali works it has become the practice to convey the waste in barges to the entrance of Loch Long and there discharge it. The result was great dissatisfaction on the part of residents on the shores of the Loch and of the fishermen. The Inspector found that the Alkali Act did not give him the power to interfere. On remonstance, however, the proprietors of the works discontinued the practice. The greater importance attaches to this matter, since it proposed to convey the sewage-sludge of London out to sea, and deposit it there.

The Inspector points out, as he did in the Report for 1887, certain grave anomalies and inconsistences which greatly interfere with the working of the Act. He proposes the following schedule of substances, the escape of which should be put under restriction:—"The acid compounds of chlorine, fluorine, sulphur, and nitrogen chlorine, and metallic fumes." We should suggest in place of "the acid compounds," all "volatile compounds."

The Report before us will doubtless satisfy all competent judges of the thorough efficiency of the Inspectors.

Electro-Metallurgy, Practically Treated. By Alexander Watt. Ninth Edition, Enlarged and Revised, with additional Illustrations and including the most Recent Processes. London: Crosby Lockwood and Son.

This volume forms one of "Weale's Rudimentary Series," issued by the eminent firm of technological publishers whose name we find on the title-page. Concerning a work which has reached its ninth edition little can be said by the reviewer, since, if it did not meet the requirements of a large number of persons it would by this time have dropped out of notice.

The author touches upon the difficult question of removing the tin from tinners' waste. On this subject not a few inventors have tried their skill, some using purely chemical and some electrical processes. The author doubts, however, and that not without reason, whether any of them have met with absolute success. It is required to obtain the tin absolutely free from iron, and the residual iron as free from tin, and to effect this separation "at a price." We believe that a company has been formed not long ago for working one of the new methods of separation on the large scale, but we do not know whether it has been successful.

The author gives a process for the preparation of potassium cyanide. We scarcely think that an electro-metallurgist, unless his operations are conducted on a very large scale, will find any advantage in producing cyanide for his own use. The same caution applies still more forcibly to the preparation of caustic soda and potassa, both of which may now be bought in small quantities.

We find from this work that according to a reprehensible trade usage articles manufactured from gold and "metal," united and rolled out into thin sheets, are spoken of as "fine gold." The author advises the electro-gilder to make himself acquainted with the various kinds of spurious gold occurring in commerce. He once placed two "gold" Albert chains in a jar of nitric acid, and, on returning in an hour to the gilding room, he found that the chains had disappeared except a thin shell of one of the links and a dark brown powder at the bottom of the jar. These chains, which had been invoiced at 55s. 6d. each, wholesale price, were merely plated metal!

A fact not generally known and here mentioned is that potassium cyanide has a very destructive action upon gutta-percha.

As the applications of electricity in metallurgy are extending this volume is likely to prove of increasing interest.

The Chemistry of the Coal-tar Colours. Translated from the German of Dr. R. Benedikt, and Edited, with Additions by E. Knecht, Ph.D., F.I.C., Head Master of the Chemistry and Dyeing Department of the Technical College, Bradford; Editor of the *Journal of the Society of Dyers and Colourists*. Second Edition, revised and enlarged. London: G. Bell and Sons.

That a second edition of this book has been called for within three years is doubly satisfactory, proving, on the one hand the value of the work, and on the other the increase of an intelligent interest felt in the scientific principles of the industrial arts.

The present edition has been greatly extended. This change is in part necessitated by the discovery of a number of new colours. If we compare the index of the first edition with that of the present volume we shall see that this increase is considerable. The author, however, is of opinion that "of all the artificial dye-stuffs at present in use there are, perhaps, only a few, especially those which are distinguished by their superior fastness, that will maintain a permanent position in dyeing."

The author evidently does not agree with the school of neo-esthetics—shall we say pseudo-esthetics?—who admire impure colours. It must be admitted, however, that the pure colours now being obtained by refined chemical procedures require much greater judgment to bring them into harmonious combinations than do the "subdued" shades which are at present so much in fashion. It has even been suggested that our sense-perceptions are entering upon a process of degradation; witness the rage for bitter flavours, for Wagnerian music, and for the "modes" and terra-cottas which are everywhere encountered.

We have hopes that Dr. Knecht's book will aid in bringing a much-needed reform, both in the manufacture of dyes in this country, and in their application. But after all, until examinationism and "payment by results" are dethroned in our colleges and technical schools we shall be more fruitful in men who can talk about processes and results than in those who can bring them to pass.

The Retrospect of Medicine: A Half-yearly Journal, containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by James Braithwaite, M.D. (Lond). Vol. xcix., January to June, 1889. London: Simpkin, Marshall, and Co.

This issue contains but little matter of which we can presume to take cognisance. Creoline—a coal product—seems to be attracting notice as a germicide. It is found to be a stronger antiseptic than carbolic acid, and as a deodorising agent it is better than either carbolic acid or mercuric chloride.

Dr. Raudnitz recommends the sterilisation of milk at the time of milking. Such milk, after being kept at the ordinary temperature of a room for three weeks, remained alkaline, and could not be distinguished from freshly drawn milk either by taste, odour, or appearance. Since Dr. Raudnitz introduced it among his patients he has seen no cases of diarrhœa.

In a paper on lead-poisoning, of which several cases have lately occurred in the North of England, Mr. Norman Porrit concludes that alcohol has a very powerful effect in intensifying the effects of lead.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 3, July 15, 1889.

Thermic Researches on the Isomeric Nitrocamphors and on Cyano-camphor. — M. Berthelot and P. Petit.—The authors investigate the thermochemical signification of the camphenic derivatives, especially as regards the isomeric nitro-compounds, the function of which is connected on the one hand with the nitric ethers of the fatty series, properly so-called, and on the other to the nitro-phenols of the aromatic series.

The Reactions of the Oils with Silver Nitrate.—Raoul Brullé.—If we treat 10 c.c. of an oil with 0·5 c.c. of fuming nitric acid in a porcelain capsule and heat the mixture with brisk stirring until froth appears, different colourations are produced according to the oil used. The treatment is continued, adding 5 c.c. of a solution of silver nitrate at 2½ per cent in alcohol at 90 per cent. If we continue heating there comes a moment, about 115°, when the silver nitrate is suddenly decomposed and metallic silver is deposited. We continue heating so as to let the first reflections disappear, and we observe on the sides of the capsule the colour of the thin oily layer seen on inclining the capsule and the metallic reflections on the surface of the liquid. On saponifying the oils and treating them in the same manner we obtain quite different colours, as obtained in the table:—

1. *In the Natural State.*

Oil.	Oily Layer.	Reflection.
Olive.	Olive green.	Green.
Cotton.	Green.	Ash green.
Sesame.	Chrome green.	Light Sèvres blue.
Earthnut.	Yellowish green.	Emerald green.
Camelina.	Persian lake.	Light blue.
Linseed.	Dragon's blood.	Emerald green.
Colza.	Persian lake.	Cyprus green.

2. *When Saponified.*

Oil.	Oily Layer.	Reflection.
Olive.	Mars orange.	Cyprus green.
Cotton.	Terra di Sienna.	Cobalt violet.
Sesame.	Gold yellow.	Cobalt violet.
Earthnut.	Persian lake.	Light violet.
Camelina.	Deep chrome.	Blue.
Linseed.	Black.	Green.
Colza.	Burnt carmine.	Ultramarine.

The names of the colours are those used by artists in water-colours.

The Decomposition of the Sulpho-conjugated Acids by Means of Phosphoric Acid.—C. Friedel and J. M. Crafts.—The former processes for the regeneration of an aromatic hydrocarbon from its sulpho-conjugated compound turned on the action of hydrochloric acid, or, as proposed by Messrs. Armstrong and Miller, of sulphuric acid in a current of steam at 170°. The authors, after explaining the defects of both these methods, propose to mix the sodium or potassium salt of a sulphuric acid with a considerable excess of phosphoric acid at 60° B.

On the Brownian Movement.—M. Gouy.—The author concludes that the pedetic movement is the only physical phenomenon which renders visible a constant internal state of agitation in bodies in the absence of any outward cause.

The Electrolysis of Distilled Water.—E. Duter.—This paper will be inserted in full.

On the Ammonio-cobaltic Molybdates, Tungstates, and Vanadiates. Separation of Cobalt and Nickel and of the Cobaltous and Cobaltic Salts.—Adolphe Carnot.—(See p. 54).

New Derivatives of Camphor.— A. Haller.—This paper does not admit of useful abstraction.

The Simultaneous Determination of Saccharose and Raffinose in Commercial Products.—L. Lindet.—This memoir also cannot be abridged.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 8 and 9, 1889.

Researches from the Laboratory of the University of Freiburg.—These include papers on tolunitranilic acid and some derivatives of hydrotoluquinone, by Fr. Kehrmann and R. Brasch; on iodophenolsulphonic acid and iodoquinon by Fr. Kehrmann; and on chlorobromoparaxylols and some of their derivatives by C. Willgerodt and R. Wolfien.

Contributions to a Knowledge of the Modifications of Cadmium Sulphide produced in the Moist Way.—N. von Klobukow.—Cadmium sulphide obtained in the moist way varies in colour from a light yellow to a deep reddish brown. Formerly the differences of colour and the modifications in density were ascribed to a difference in chemical composition. It appears, however, from the comprehensive investigations of Follenius and Buchner that in aqueous solutions of cadmium there is formed only one grade of sulphuration, cadmium monosulphide, and that the precipitates of different colours have the same empirical composition. The author concludes that the determination of the sp. gr. of the modifications of cadmium sulphide described by Buchner speaks in favour of their isomeric character. Crystallographic examination leads to the same result, and renders it probable that there exist more than two modifications of cadmium sulphide. The mutual transformation of the modifications of cadmium sulphide can be effected not merely by the action of heat and of various chemical agents, but by friction, pressure, and by means of nascent hydrogen.

On the Fission-products of Casein.—E. Drechsel.—In this preliminary notice the author raises the questions:—If all the albumenoids, on treatment with strong hydrochloric acid, yield identical bases, do animal and vegetal albumenoids behave identically or not? What is the relation of these bases to the ptomaines?

Researches from the Laboratory of Prof. Saytseff at Kasan.—These researches comprise:—Action of iodmethyl and zinc upon ethyl-propyl-keton, by E. Sokoloff; action of iodethyl and zinc upon ethyl-propyl-keton, by E. Sokoloff; examination of the hydrocarbons C_8H_{16} and C_9H_{18} from methyl-dipropyl-carbinol and ethyl-dipropyl-carbinol, by E. Sokoloff; action of iodethyl and zinc upon malonic ethyl-ether, by St. Joukowsky; action of iodallyl and zinc upon malonic ethyl-ether, by W. Matweeff.

On Certain Ferrocyanides.—C. Rammelsberg.—The author describes lead ferrocyanide with the modifications obtained by Zepharovich, Gintl, and Wyrouboff, barium, hydrogen, and silver ferrocyanides.

Libel on a Chemist.—The Press of Paris, and in particular the *XIX Siècle*, have lately brought against M. Charles Girard, the Director of the Municipal Laboratory, charges of incapacity and of accepting bribes. Girard, in consequence, took proceedings for libel. The editor of the *XIX Siècle* has been condemned to one month's imprisonment, a penalty of 1000 francs, and to pay the plaintiff 15,000 francs damages.—*Chemiker Zeitung.*

THE CHEMICAL NEWS.

Vol. LX. No. 1550.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

(Concluded from p. 53).

Action of Different Earths on Phosphorescence Spectra.

Another modification of phosphorescence spectroscopy is produced by the previous addition of other earths to the specially phosphorescent earths, and of the results of such addition some instances have already been mentioned. Lime exerts in this manner a remarkable action. By itself it phosphoresces with a continuous spectrum, after the fashion of yttria with a discontinuous spectrum. If, however, they are mixed, the phosphorescing energy of the lime does not extend over the whole spectrum, but concentrates itself on strengthening the yttria bands. These bands become broader, but also less definite, in proportion as the lime increases in quantity.

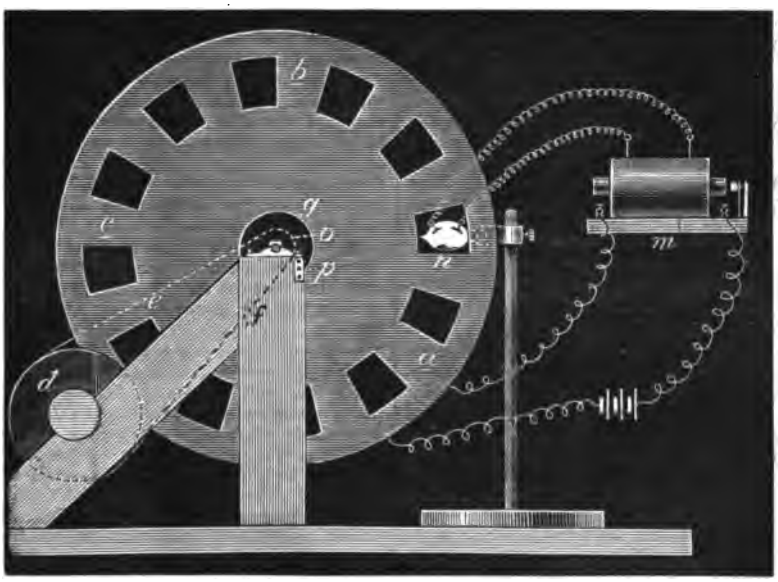
Lime also may be made to play a useful part in bringing out the phosphorescent bands of samaria. The bands are not so numerous as those of yttrium, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, the samarium spectrum is seen to consist of three bright bands—red, orange, and green — nearly equidistant, the orange being brightest. With a narrower slit the orange and green bands are seen to be double. (Fig. 18).

The addition of lime also affords an argument for the compound nature of samaria, as it suppresses the sharp line Sδ, the most striking feature in the phosphorescence spectrum shown by pure samarium sulphate. On the other hand, an addition of old yttria deadens the other lines of samaria, but brings out the line Sδ more strongly. Fig. 19 represents the spectra given by the meta-elements of samarium.

Lanthanum sulphate in the radiant matter tube phosphoresces with a reddish colour and has a broad hazy band in the orange, with a sharp line superposed. This line is identical with the line of Gε, one of the components of the phosphorescent spectrum of samarium. If lime is added to lanthanum, the phosphorescence changes its colour from red to yellow. Lime also brings out the lines of yttrium and samarium if they are present as impurities. When Gδ, Gα, and Gβ are present in small proportions with lime, the lines Gδ and Gα become intensified, but a dark place appears in place of the green Gβ band. Hence it appears that if only a small trace of Gβ is found with lime and lanthanum, the green line is not only obliterated, but the quenching action suppresses that part of the continuous lime spectrum which has the same refrangibility as the Gβ line, thus giving a black space in the spectrum.

A specimen of lanthana thrown out in a fractionation of didymia, examined in the radiant matter tube, phosphoresces of a yellow surface-colour and gives an extremely brilliant spectrum (Fig. 20). In the red there is a very fine and sharp line, somewhat like the alumina line, but nearer C of hydrogen. Then come a couple of misty red lines, the first apparently compound, then a hazy pair of green lines, and finally another wide apart pair of a bluish green; the first of these lines is intensely brilliant.

Fig. 22.



Interference of Phosphorescence Spectra.

I have already frequently noted the modification induced in the normal spectrum of one earth by the mixture of various quantities of others, when treated as anhydrous sulphates, and of these one of the most striking is seen in the case of a mixture of samaria with yttria, since the presence of even 40 per cent of yttria practically obliterates its spectrum. The most minute proportion of

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

lime added to samaria causes the sharp line at $1/\lambda^2$ 269 in its spectrum to vanish, at the same time greatly intensifying the other bands. Strontia, baryta, glucina, thoria, magnesia, lanthana, alumina, and oxides of zinc, cadmium, lead, bismuth, and antimony, all give characteristic spectra with samaria, and have been fully described in my paper on that body (*Phil. Trans.*, Part II., 1885). The action of lime upon yttria is of great use in detecting very small quantities of this earth when in combination with other elements which otherwise would prevent its phosphorescence.

A recent discovery of some beautiful spectra given by the rare earths when their pure oxides are highly calcined, shows the remarkable changes produced in the spectra of these earths when two or more are observed in combination. It has likewise opened to me a wide field of investigation in the nature of the elements themselves. Alumina is especially active in inducing new spectra when mixed with the rare earths. I have given more than a twelvemonth to the exclusive study of alumina phosphorescence, and still the research is incomplete. But I have obtained some remarkable results. A moderate amount of fractionation has enabled me to penetrate below the surface of the red glow common to crude alumina, and to see traces of a most complicated sharp line spectrum. By pushing one particular process of fractionation to a considerable extent, I have obtained evidence of a body which is the cause of some of these lines. The spectrum described by me in 1887 (CHEM. NEWS, lvi., 62, 72) is one of great beauty, and a fair idea of it is given in Fig. 21. The new body is probably one of the rare elements or meta-elements closely connected with decipia, for I have reproduced the spectrum very fairly by adding decipia to alumina. Before arriving at definite conclusions much time must be devoted to the subject. Certain it is that this new earth is not yttria, erbia, samaria, didymia, lanthana, holmia, thulia, gadolinia, or ytterbia, the spectrum of each of these when mixed with alumina being very beautiful, but differing entirely from the decipia-alumina spectrum. Some of these new spectra are shown in Fig. 29.

The Phosphoroscope.

The phosphoroscope affords another method of verifying the simple or compound character of a substance. It is well known that the continuance of phosphorescence after the cessation of the exciting cause varies widely, from some hours, as in the case of the phosphorescent sulphides, to the fraction of a second in the case of uranium glass and quinine sulphate. On examining phosphorescent earths glowing in a vacuum tube under the action of the induction discharge, I found remarkable differences in the duration of this residual glow. Some of the earths, after the cessation of the current, remain luminous for an hour or more, whilst others cease to phosphoresce immediately on the stoppage of the current. Take the case of yttrium. As already stated, I succeeded in resolving this earth into several simpler bodies not equal in basicity. While seeking for further proof of the distinct character of these bodies I observed that the after-glow differed somewhat in colour from that which the earth exhibited whilst the current was still passing. Further, the spectrum of the after-glow seemed to show, so far as I could judge by the faint light, that some of the lines were missing. As this phenomenon indicated another difference among the components of yttrium, I examined them in an instrument similar to Becquerel's phosphoroscope, but acting electrically instead of by means of direct light.

Without describing this apparatus, shown in Fig. 22, I may mention some of the results obtained by its use. Under ordinary circumstances it is scarcely possible to perceive any phosphorescence in an earth until the vacuum is so high that the line spectrum of the residual gas begins to grow faint. Up to this point, the stronger light of the glowing gas overpowers the feeble glow of the phosphorescence. But in the phosphoroscope the light of the glowing gas lasts only for an inappreciable time, while that of the phosphorescent earth persists long enough to be distinctly observed. The different bands of the new constituents of yttria do not all appear at the same speed of rotation. At the lowest speed the double greenish blue band of $G\beta$ is first seen, followed next by the dark blue band of $G\alpha$. As the velocity increases there follows the bright citron-yellow band of $G\delta$, and as the utmost speed approaches the red band of $G\zeta$ is seen, but with difficulty. If lanthanum sulphate along with a little lime is examined in the phosphoroscope the line of $G\varepsilon$ is visible at the lowest speed; $G\delta$ follows at an interval of 0·0035 second, and the $G\alpha$ line immediately aftewards.

M. de Boisbaudran's Reversion Spectra.

Another modification of the phosphorescence process is afforded by the "reversion spectra" of M. Lecoq de Boisbaudran.

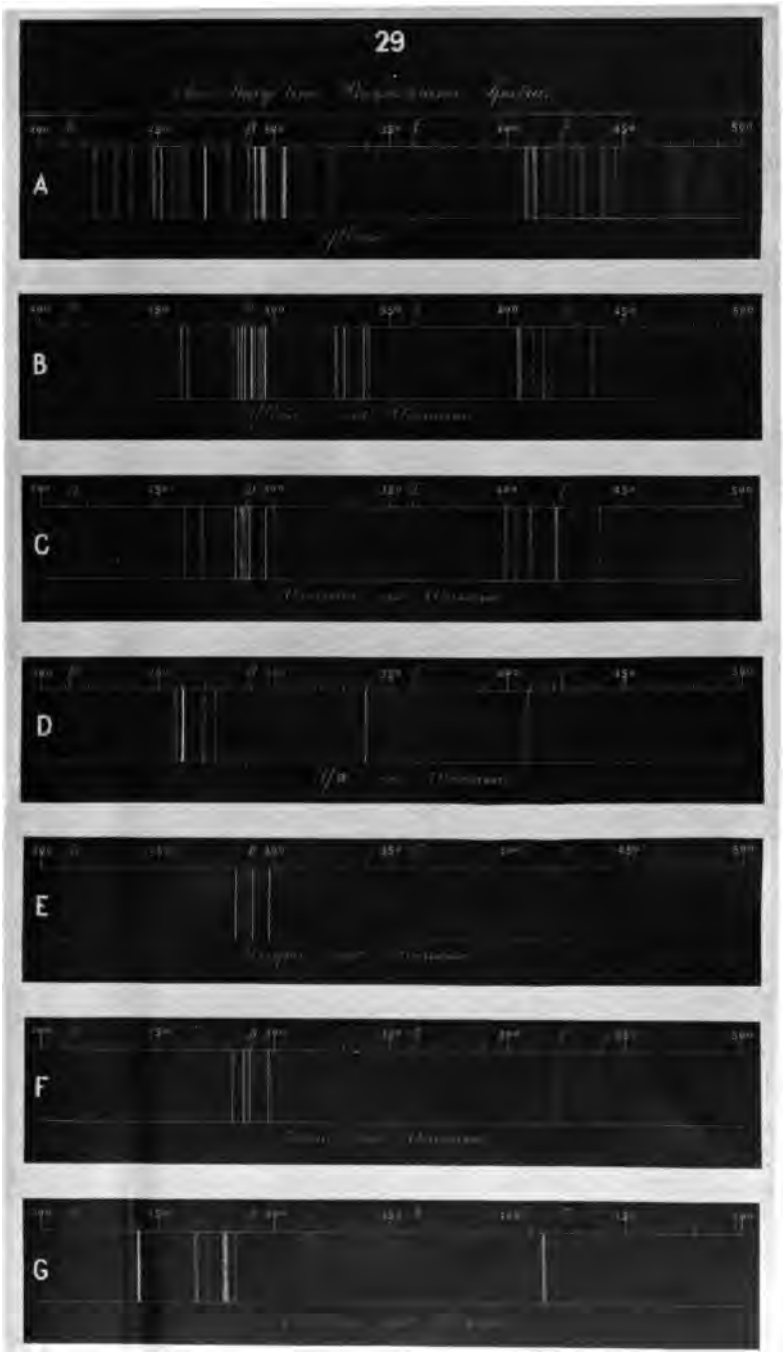
The following is the description of this process by M. Lecoq de Boisbaudran, read before the Academy of Sciences on June 8th, 1885:—"When the electric spectrum of a solution *with a metallic base* is produced it is customary to make the outside platinum wire (whence the induction spark strikes) positive, the liquid consequently forming the negative pole. If the direction of the current is reversed the metallic rays (due to the free metal or to one of its compounds) are scarcely or not at all visible; at all events, so long as the exterior platinum wire now forming the negative pole is not coated with a deposit." Fig. 15 shows the arrangement. M. de Boisbaudran continues:—

"Having again taken up last year my researches on the rare earths belonging to the didymium and yttrium family, I had occasion to observe with many of my preparations the formation of spectrum bands, nebulous, but sometimes tolerably brilliant, having their origin in a thin layer of a beautiful green colour, which appeared at the surface of the liquid (a solution of a chloride) when it was rendered positive."

M. de Boisbaudran further adds:—"The production of my reversion spectrum appears to be analogous physically with the formation of the phosphorescence spectra obtained by Mr. Crookes at the negative pole in his high vacuum tubes containing certain compounds of yttria. The conditions of the two experiments are, however, practically speaking, very different."

By this method M. de Boisbaudran has discovered phosphorescent spectra, shown in Figs. 23 and 24, which he considers due to the presence of two earths, one of which, supposed to be new, he has provisionally named $Z\alpha$, and another, also thought at first to be new, and therefore called $Z\beta$, but since admitted by him to be terbia (*Compt. Rend.*, cviii., 167, Jan. 28, 1889). In the hands of so skilful an experimentalist as my accomplished friend, this method may give trustworthy indications, but the test is really beyond the range of practical analysis, owing to the difficulty of eliciting the phenomena. Unless the strength of the spark, the concentration and acidity of the solution, and the dispersive and magnifying power of the spectroscope bear a certain proportion to each other, the observer is likely to fail in seeing a spectrum even in solutions of earths which contain considerable quantities of $Z\alpha$ and terbia.

I have had not only the advantage of personal instruction in Paris from M. de Boisbaudran himself in the best methods of getting these reversion spectra, but I secured some of the identical earths which give these spectra most distinctly. Yet with all these advantages I have experimented for hours together without being able to see more than a feeble glimmer of the bands described by M. de Boisbaudran. Moreover, the bands of these "reversion" spectra, at their strongest, are but faint and hazy substitutes for the brilliant lines of yttria seen by the "bombardment" process, and they do not even in all cases agree with them in position. M. de Boisbaudran,



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.

speaking of the relative sensitiveness of our two processes, admits that the bombardment process *in vacuo* is incomparably more delicate than his reversion method. My own estimate of the relative sensitiveness of the two methods is in the proportion of at least 1 : 100. Though so accurate an observer, M. de Boisbaudran concluded apparently too hastily that two spectra are identical, when one of them has been measured only approximately, and contains bands in positions which are perfectly blank in the other.

The Phosphorescence of Alumina.

I now wish to draw attention to some recent researches on the phosphorescence spectrum given by alumina. So far back as 1859 Becquerel examined in his phosphoroscope pure alumina carefully prepared, and described it as glowing with a splendid red colour. He rendered his specimens phosphorescent by exposure to the sun, and made no use of the induction spark. As described by Becquerel (*Ann. Chem. Phys.*, lvii., 50, 1859), the spectrum of the red light emitted from alumina agrees with that of the ruby when submitted to the radiant matter test. It displays one intensely red line a little below the fixed line B in the spectrum, having a wave-length of about 689·5. There is a continuous spectrum beginning at about B and a few fainter lines beyond it, but in comparison with this red line the faint ones are so dim that they may be neglected. My latest observations in the vacuum tube prove this line to be double, the distance apart of the components being about half the distance separating the D lines (*Proc. Roy. Soc.*, xlii., 26, Dec. 30, 1886), their respective wave-lengths being 694·2 and 693·7 ($1/\lambda^2$ 207·5 and 207·8). This alumina spectrum is shown in Fig. 25.

The red phosphorescence of this alumina is exceedingly characteristic. M. de Boisbaudran (*Compt. Rend.*, ciii., 1107; civ., 330, 478, 554, 824) contends, however, that this red phosphorescence is due not to the alumina itself, but to an accompanying trace of chromium, $\frac{1}{1000}$th part of chromium being sufficient to give a splendid red phosphorescence, whilst even 1 part of chromic oxide in 10,000 will produce a very distinct rose colour. In testing this view I have purified alumina most carefully, so as to secure the absence of chromium, and on examining it in the radiant matter tube I have still obtained the characteristic phosphorescence and spectrum. I have then added to my purified alumina chromium in known varying proportions, but without finding any increase in the intensity of the phosphorescence. I fractionated my purified alumina by different methods and found that the substance which forms the crimson line becomes concentrated towards one end of the fractionations, whilst chromium concentrates at the other end. I have suggested four possible explanations of the phenomena—

1. The crimson line belongs to alumina, but it is liable to be masked or extinguished by some other earth, which accumulates towards one end of the fractionations.

2. The crimson line is not due to alumina, but to the presence of an accompanying earth, which accumulates towards the other end of the fractionations.

3. The crimson line belongs to alumina, but its development requires certain precautions to be taken in the duration and intensity of the ignition, and absolute freedom from alkaline and other bodies carried down by precipitated alumina, and difficult of removal by washing.

4. The earth alumina is a compound molecule, one only of its component sub-molecules giving the crimson line. If this hypothesis is correct, alumina must admit of being split up in a manner analogous to yttria.

Sharp Line Spectra with Phosphorescent Alumina.

About eighteen months ago M. de Boisbaudran published some results on "New Fluorescence with well-defined Spectral Rays" (*Compt. Rend.*, cv., 258). Having mixed alumina with 2 per cent of samaria and converted the mixture into sulphate, he heated it to a temperature between the melting-point of copper and silver. This product, examined in the radiant matter tube, gives a faint fluorescence, the spectrum resembling the samarium-aluminium spectrum described by me in June, 1885 (*Phil. Trans.*, Part II., 1885, 712) (Fig. 26). That is, aluminium and samarium give a spectrum resembling the corresponding calcium-samarium one as to the red and the double orange, but having a very broad, rather faint, green band with a black division in the middle occupying the position of the bright green band of calcium-samarium.

On submitting this aluminium-samarium mixture to a very high temperature, M. de Boisbaudran finds that its spectrum alters greatly. In place of the three nebulous bands, there are now a number of sharp rays forming three groups corresponding respectively to each of the three diffused bands above described.

This spectrum seems to me closely to resemble the complicated system of sharp lines shown by alumina after moderate fractionation, to which I have already referred (Fig. 27, lower spectrum). Taking some of this alumina, I added to it one-fiftieth of its weight of samaria, and thereby obtained a spectrum similar to that described by M. de Boisbaudran (Fig. 27, upper spectrum). As I had suspected, the two spectra are almost identical; the effect of the samaria is simply to intensify some of the lines and weaken others. But between this sharp line high temperature spectrum and the band spectrum (Fig. 26) given by the same mixture treated at a lower temperature I fail to see any such resemblance as could support the view that the groups correspond save that "those of the line spectra are less refrangible." The explanation of M. de Boisbaudran's result is simple. Both samarium sulphate and aluminium sulphate resist a red heat without their sulphuric acid being driven off. Aluminium sulphate does not phosphoresce, samarium sulphate does, therefore the mixture gives the samarium spectrum. But if the mixed sulphates are heated to the highest blowpipe temperature both are decomposed, and there is left a mixture of samaria and alumina. Now, samaria by itself gives no phosphorescence spectrum, but alumina gives the new line spectrum I have described.

This method is applicable only when the earths are in a sufficiently high state of purity. The presence of exceedingly small traces of other matter may greatly modify the spectrum.

Conclusions.

During the course of the investigations—whose results are briefly summarised in the foregoing pages,—I have repeatedly had recourse to the balance, to ascertain how the atomic weights of the earths under treatment were varying. An atomic weight determination is valuable in telling when a stable molecular grouping is arrived at. During a fractionation, the atomic weight of the earth slowly rises or falls until it becomes stationary, after which no further fractionation of that lot *by the same process* makes it vary. Usually a result of this kind has been relied on as proof that the elementary stage has been reached. This constancy of atomic weight, however, only proves that the original body has been split up by the fractionating process into two molecular groupings capable of resisting further decomposition by that identical process; but these groupings are not unlikely to break up when a different fractionating process is brought to bear on them, as I found in the separation of didymium and samarium when using dilute ammonia as the fractionating precipitant. In my paper on "Radiant Matter Spectroscopy" I said*:—"After a time a balance seems to be established between the affinities at work, when the earth would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them,

* Part II., Samarium," *Phil. Trans.*, Part II., 129, June 18, 1885.

when fractionation by ammonia could be again employed."

It is obvious that when the balance of affinities here spoken of was reached, the atomic weight of the mixture under treatment would have become constant, and no further fractionation would have caused the atomic weight to alter.

Atomic weight determinations are valuable in telling when the fractionating operation in use has effected all the separation it can: at this point it becomes constant. The true inference is, not that a new earth has been obtained, but simply that the fractionating operation requires changing for another, which will cleave the group of meta-elements in a different direction.

Meantime, I have kept strictly in view the question, What is an element, and how shall it be recognised when met?

On this subject I beg to submit the following considerations, which, primarily referring to didymium, may at any moment apply to other cases:—

Neodymium and praseodymium are simply the products into which didymium is split up by one particular method of attack.

It must be remembered that a single operation, be it crystallisation, precipitation, fusion, partial solution, &c., can only separate a mixture of several bodies into two parts, just as the addition of a reagent only divides a mixture into two portions, a precipitate and a solution, and these divisions will be effected on different lines according to the reagent employed. We add, *e.g.* ammonia to a mixture, and at once get a separation into two parts. Or we add, say, oxalic acid to the same original solution, and we then split up the mixture into two other parts differently arranged.

Thus by crystallising didymium nitrate (in Auer's way) we divide the components into two parts. By fusing didymium nitrate we divide its components in a different way; but so long as different methods of attack split up a body differently, it is evident that we have not yet got down to "bed rock."

Further, a compound molecule may easily act as an element. Take the case of didymium, which is certainly a compound, whether the products of Auer's operation be final or not. Didymium has a definite atomic weight; it has well-defined salts, and has been subjected to the closest scrutiny by some of the ablest chemists in the world. I refer particularly to Clève's classical memoir. Still the compound molecule known as didymium was first too firmly held together to act otherwise than as an element, and as a seeming element it emerged from every trial. The simple operations to which it had been submitted in the preparation of its salts, and in its purification from other compound molecules, such as samarium and lanthanum, were not sufficient to split it up further. But subjected to a new method of attack it decomposes at once.

We have, in fact, a certain number of reagents, operations, processes, &c., in use. If a body resist all these and behave otherwise as a simple substance, we are apt to take it at its own valuation, and to call it an element. But for all that, it may, as we see, be compound, and as soon as a new and appropriate method of attack is devised we find it can be split up with comparative ease. Still, we must never forget that, however complex, it can hardly be resolved into more than two parts at one operation.

From considerations above laid down I do not feel in a position to recognise neodymium and praseodymium as elements. We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed, and to this point I must beg to call the special attention of my colleagues. It may be that whatever body gives only one absorption-band is an element, but we cannot conversely say that an element may be known by its giving only one absorption-band, since most of our elements give no bands at all!

Until these important and difficult questions can be decided, I have preferred to open what may be figuratively called a suspense account, wherein, as I have previously suggested, we may provisionally enter all these doubtful bodies as "meta-elements."

But these meta-elements may have more than a mere provisional value. Besides compounds, we have hitherto recognised merely ultimate atoms, or the aggregations of such atoms into simple molecules. But it becomes more and more probable that between the atom and the compound we have a gradation of molecules of different ranks, which, as we have seen, may pass for simple elementary bodies. It might be the easier plan, so soon as a constituent of these earths can be found to be chemically and spectroscopically distinguishable from its next of kin to give it a name, and to claim for it elemental rank; but it seems to me the duty of a man of science to treat every subject, not in the manner which may earn for him the greatest temporary κῦδος, but in that which will be of most service to Science.

If the study of the rare earths leads us to clearer views on the nature of the elements, neither my colleagues nor myself will, I am sure, regret the months spent in tedious and apparently wearisome fractionations. No one can be more conscious than myself how much ground is yet uncovered, and how many radical questions have received but very inadequate answers. But we can only work on, "unresting, unhasting," trusting that in the end our work will throw some white light upon this deeply interesting department of chemical physics.

THE MOLECULAR WEIGHTS OF SOME POLYMERIC COMPOUNDS AS DETERMINED BY RAOULT'S METHOD.

By RAPHAEL MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C.

In the course of some investigations upon the diazoamido-compounds we have recently had occasion to determine the molecular weights of some compounds which, on purely chemical grounds, we had undoubted evidence to show consisted of molecules having double the weight usually assigned. Notwithstanding the chemical evidence, which will be given in a future communication, the molecular weights, as determined by Raoult's method, came out one-half the value required by our formulæ. A precisely similar experience has recently been recorded by Anschütz (*Ber.*, 1889, p. 980) with respect to the dimethyl-ether of diacetylracemic acid. It became of interest, therefore, to examine into the method itself with a view to ascertaining how far it was applicable to the determination of the molecular weights of polymerides. Since this subject has of late excited a great deal of interest, we are induced to make known our results as a contribution to the discussion. The compounds with which we have experimented are aldehyde, paraldehyde, and metaldehyde. The first solvent tried was benzene, because this is the solvent which we had actually to employ for the diazoamides. A specimen of perfectly pure benzene was kindly supplied for our purpose by Messrs. Read Holliday and Sons, of Huddersfield. The method of working the process, and the form of apparatus, are now well known, and require no special description. The usual symbols have been adopted, viz.:—

E, for the observed "setting point" of the solution; the thermometer scale being read off by means of a cathetometer.

C, for the *depression* of freezing-point.

A, for the "coefficient of depression," *i.e.*, the depression of freezing-point produced by 1 grm. of the substance in 100 grms. of the solvent.

M, for the molecular weight calculated from the foregoing values.

I. *Aldehyde*, C_2H_4O, Mol. Wt. 44.

Freezing-point of benzene 5·30, strength of solution 0·4169 grm. aldehyd in 61·81 grms. solvent.*

E.	C.	A.	M.
4·70	0·60	0·889	55
4·70	0·60	0·889	55

Added 0·3710 grm.; total 0·7879 grm.

E.	C.	A.	M.
4·15	1·15	0·902	54
4·15	1·15	0·902	54

Added 0·2239 grm.; total 1·10118 grms.

E.	C.	A.	M.
3·90	1·40	0·855	57
3·90	1·40	0·855	57

II. *Paraldehyde in Benzene*, Mol. Wt. 132.

Freezing-point of benzene 5·3, strength of solution 0·5819 paraldehyde in 66 grms. solvent.

E.	C.	A.	M.
4·98	0·32	0·363	135
4·98	0·32	0·363	135

Added 0·7462 grm.; total 1·3281 grms.

E.	C.	A.	M.
4·53	0·77	0·383	128
4·53	0·77	0·383	128

Added 0·8544 grm.; total 2·1825 grms.

E.	C.	A.	M.
4·05	1·25	0·378	129·6
4·05	1·25	0·378	129·6

Metaldehyde is practically insoluble in benzene, but soluble to some extent in acetic acid, so experiments were next conducted with this solvent.

III. *Paraldehyde in Acetic Acid.*

Freezing-point of acid 16·0, strength of solution 0·8967 grm. in 79·64 grms. solvent.

E.	C.	A.	M.
15·70	0·30	0·266	146
15·70	0·30	0·266	146

Added 1·179 grms.; total 2·0757 grms.

E.	C.	A.	M.
15·25	0·75	0·288	135
15·27	0·73	0·281	138·7

Added 0·4162 grm.; total 2·4919 grms.

E.	C.	A.	M.
15·10	0·90	0·288	135
15·10	0·90	0·288	135

IV. *Metaldehyde in Acetic Acid.*

Freezing-point of acid 16·0, strength of solution 0·1176 grm. in 63·11 grms. solvent.

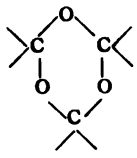
E.	C.	A.	M.
15·90	0·10	0·5366	72·6
15·90	0·10	0·5366	72·6

Metaldehyde is so insoluble in acetic acid that it was not found possible to work with solutions stronger than the above, as the substance crystallised out on cooling down the acid.

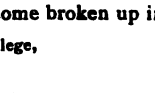
Our experiments have not been conducted with a sufficiently large number of polymeric compounds to warrant any general discussion of the results. As far as they go, it would appear that the method enables us to distinguish between C_2H_4O and $C_6H_{12}O_3$. The results for aldehyde are somewhat high, but it is not certain that the specimen employed, although purchased as pure, may not have contained some polymeride. The result for metaldehyde is abnormal and agrees approximately with—

$$C_2H_4O + \frac{C_2H_4O}{2};$$

mol. wt. 66. Paraldehyde in water gave quite irregular results, probably owing to the chemical action of the solvent. We can fully confirm the statement of Beckmann (*Zeit. f. Phys. Chem.*, ii., 715) that benzene is the solvent which offers the greatest facilities of manipulation. Although the experiments seem to indicate that the molecular weights of polymerides, such as aldehyde and paraldehyde, can be determined by the method of Raoult, we do not think that it is a legitimate deduction to infer that the method is universally applicable to all cases of polymerism. We have, as previously stated, distinct evidence to the contrary with diazoamides, and we may further point to the apparent failure of the method in the case of metaldehyde, which certainly cannot have a smaller molecular weight than paraldehyde. The whole question is, however, complicated by the possible chemical action of acetic acid upon metaldehyde, and we propose to repeat the determination with some other solvent, if a suitable one can be found. There can be but little doubt that in the case of polymerides the stability of the molecule in the solvent determines the success or failure of the method. Thus, paraldehyde may contain the nucleus*:—



which may be fairly stable, while the mixed diazoamides contain the unstable ring†:—



which may easily become broken up in solution.

Finsbury Technical College,
July 20, 1889.

* The aldehyde was weighed in small, thin glass bulbs, which were broken after introduction into the solvent.

* See, for instance, Strecker and Wislicenus, "Text-book of Organic Chemistry," p. 261.

† *Journ. Chem. Soc. Trans.*, 1889, p. 443.

NOTE ON THE ARSENICAL WATER OF COURT ST. ETIENNE (BELGIUM).

By Dr. T. L. PHIPSON, F.C.S., &c., London,
Formerly of the University of Brussels.

In 1872 died J. T. Liboutton, for the previous forty-two years burgomaster of the little town of Court St. Etienne (St. Stephen's Court) in Brabant. He left the greater portion of his fortune to the town in order that an asylum or almshouse for the aged poor might be built there. The authorities set to work without delay, and in the year 1878 the building was completed. It was called, from the name of its founder, the Hospice Liboutton. A very short time elapsed before it was observed that old people appeared to thrive there in a very remarkable manner; the bloom and freshness of youth returned more or less, replacing the dull pale tints of age; and this occurred so rapidly that it seems to have attracted general notice.

In trying to account for this singular fact the management of the Hospice came to the conclusion that it could not possibly be due to any special article of diet, for the food taken was of a very ordinary kind; nor were the

pure air of the locality and dryness of the soil considered sufficient to explain the mystery, for mystery it certainly was, and so it remained until suddenly three of the inmates of the establishment died, at very short intervals, and within six months of the opening of the Hospice. A fourth inmate retired voluntarily from the place, fearing to meet with the same fate as his three companions.

The food, the air, and the soil had been inquired into; at last attention was turned towards the water supplied to the establishment. It was found to be arsenical.

The spring issues near some lodes of mispickel (arsenical iron pyrites), and I find that this water, which is cold, bright, and clear, and has a pleasant taste, yields to analysis 19¼ grains of total residue to the imperial gallon. Of these, 0·7 grain is *arsenic acid*, and 0·84 grain ferric oxide, the remainder being composed of the usual compounds of lime, soda, silica, and magnesia, found in spring waters. It is supposed to have a constant composition, but to establish this fact it will be necessary to make another analysis at some distant date. Nevertheless it is supplied to various pharmacies, and is used in medicine as a substitute for Fowler's solution or Bourboule water from the Puy de Dôme (France). It is much richer in arsenic than the water of Mont Dore (Puy de Dôme).

Such is, in a few words, the history of the most recently discovered arsenical mineral spring. The composition of this water and the geological nature of the district—not far from the celebrated plains of Waterloo—do not indicate the most remote connection with any volcanic phenomena.

THE NATURE OF SOLUTIONS.

By S. U. PICKERING, M.A.

I BEG to announce that I have this day succeeded in isolating in the solid crystalline form one of the hydrates of sulphuric acid, the existence of which in solutions I had lately predicted from a study of the densities and heat of dissolution of sulphuric acid solutions of different strengths (*Proc. Chem. Soc.*, 1889, 88; and CHEMICAL NEWS, lix., 249). The new hydrate is $H_2SO_4,4H_2O$, containing 57·66 per cent of acid. The proof of its existence depends on its having a definite melting-point at $-25°$, which is lowered (as far as about $-70°$) by the addition of excess of either water or sulphuric acid, and on other evidence which it is not convenient to give in the present place. The isolation of one of the hydrates with either 2, 4, 5, or $9H_2O$ had been rendered probable by a study of the freezing-points of sulphuric acid solutions, and the nature of the curves representing the freezing-points of solutions from which the tetrahydrate crystallises renders it highly improbable that any other hydrate will be obtained in the solid form except, of course, the monohydrate, which has long been known. Such an absolute proof of the conclusions which I have drawn from other sources must place those conclusions beyond doubt, and must establish as an incontestable fact the existence of hydrates in solution.

July 31, 1889.

Carbolic Disinfectants.—We have received from Messrs. F. C. Calvert and Co., of Manchester, a selection of carbolic acid preparations. Their Carbolic Vaporiser is not only useful in sick rooms, but it will be found valuable for driving away gnats and other winged pests. Of similar value against gnats, flies, and mosquitoes is the Carbolic and Camphor (Anti-mosquito) Soap, with which, if a man washes himself liberally, he is supposed to pass freely through the most gnat-haunted district. The Prickly Heat Soap is useful against one of the minor inconveniences of such tropical weather as we have lately passed through, whilst the Dento-Phenolene Mouth Wash will be much appreciated by smokers.

UNIVERSITY COLLEGE, LONDON.
TECHNICAL TRAINING IN CHEMISTRY.

IT is becoming generally recognised that it is necessary, if our manufacturers are to compete on equal footing with continental rivals, to give a more complete scientific and practical training to those about to engage in business or manufactures in which a competent knowledge of chemistry and chemical technology, with its coadjutors, chemical engineering and construction, are required. A discussion at various centres of chemical industry on the training necessary for manufacturing chemists has been published in the June number of the *Journal of the Society of Chemical Industry*, and a unanimous opinion has been elicited that the day is past when a man can enter on any pursuit connected with chemistry without previously equipping himself with a thorough training in chemistry as well as in allied subjects. It is only by aid of such a complete training that the English nation can hope to compete on equal terms with foreign rivals; and without such an education no young man can look forward to engaging in manufacture with any prospect of success. It is especially necessary that firms which are looking forward to enrolling young men as partners, or who intend them to occupy higher official positions, should take steps to give them as complete an education in the necessary subjects as possible. It is an investment which certainly yields the largest possible returns both on outlay and capital.

Mr. Ivan Levinstein, of Manchester, the well-known manufacturer of chemicals and colours, has delivered the following opinion on the industrial value of technical training, under the auspices of the National Association for the Promotion of Technical Training, which he has kindly allowed us to quote:—

"Probably in no branch of chemical industry is technical instruction of greater value than in the coal-tar colour manufacture, with which I am connected, and in no branch has our progress, compared with that of some of our competitors, been more unsatisfactory. For example, the exports of coal-tar products from Germany increased from 195,380 cwts. in 1884, to 319,922 cwts. in 1887, while, as is well known, our exports in these articles have been decreasing. Although this remarkable progress on the part of Germany is, in my opinion, by no means exclusively due to the superior education of their scientific chemists, still the fact is indisputable that greater attention ought to be paid to the training of our young men who desire to enter colour works. Every year a large number of young men issue from our technical schools, who wish to find employment as chemists, the majority of whom are by no means adequately prepared for the purpose. Manufacturers continue to show a preference for German or Swiss chemists, to whom they are often willing to give much higher salaries than to men incompletely trained in our own schools. The whole of the blame of this state of things is not to be laid on our technical schools, especially the best of them; the fault lies to some extent with the parents and advisers of these young men, who, in entire ignorance of what is really required in these days of progress, expect that a youth, having received a mediocre general education and spent two years at a college or technical school, ought at once to be able to earn a livelihood as a chemist in some of our works. We have already far too many of these half-trained chemists. It is not increased quantity but improved quality which we want, and unless this fact is fully recognised, the erection and establishment of new colleges and technical schools will do very little to improve our position.

"The study of chemistry is very laborious and difficult, and no youth should decide to embrace such a career, in any of its departments, unless he has the natural inclination and talent for scientific work, and the means to devote a considerable period of time to the acquisition of

a thorough knowledge of general subjects, as well as of the science to which he intends to give special attention.

"It is clear that the existence of the two first of these requisites can only be ascertained by developing science-teaching throughout our educational system.

"No difference should be made in the general and scientific education of the student, whether he intends eventually to become a teacher or a professional chemist in a manufactory or on his own account; because the ultimate choice will depend largely on circumstance and on individual capacity. It is, in my opinion, a great mistake to believe that a chemist in a manufactory or works requires less knowledge of the science than a teacher or an experimental chemist.

"Now, as regards the arrangements in the teaching institutions which profess to prepare and complete the education of chemists, I would advise that no one should be admitted as a regular or ordinary day student who has not passed a very strict and high-class examination in general subjects. Further, no certificate of efficiency should be given unless the student, after having passed the preliminary examination, has attended, for at least three years, the courses of lectures on chemistry and kindred subjects and the laboratory courses prescribed at one or other of the recognised institutions.

"By this time he will probably have made up his mind as to whether he intends to adopt the career of chemist in works, or that of an experimental or analytical chemist. In either instance he might with advantage continue his course of study for another twelve months, substituting for any subject which had no special bearing on his future work a course, say in chemical engineering and the construction of chemical plant, or, if he intends to seek employment in colour, dye, bleach, or print works, a course in dyeing, printing, and bleaching. It is obvious, however, that it is not sufficient that the youth himself should possess all the qualifications required; his successful training will naturally depend largely on the teaching staff, and it is especially to the selection of teachers of chemistry that very great attention must be devoted. They should not only be capable teachers and distinguished men of science, but should also possess talent and originality, and they should be placed in such a position as to be entirely independent of the necessity of undertaking any work which lies outside their sphere."

Perhaps the most successful school of applied chemistry in existence is that of Prof. Lunge, at the Zürich Polytechnikum. He expresses the following opinion on the necessity of education in chemical technology:—

"In my opinion a young man who aspires to the position of a works' chemist with the view of afterwards becoming practical manager of a chemical factory, should be well educated in a general way to begin with: he should have a thorough grounding in mathematics and in French and German, and, if possible, in the elements of geometrical drawing. When entering upon his proper chemical training he should begin with a purely scientific study of chemistry and physics, not forgetting mathematics, mineralogy, geology, and even biology, and he should be thoroughly taught to practise chemical analysis and to manipulate apparatus of all kinds. Later on he must learn to make even the most difficult of chemical preparations. Only when he has laid a thorough 'scientific' foundation he must begin with technology, chemical as well as mechanical, which in such disciplinary course indeed cannot be kept separate, since in chemical technology he must be made acquainted with the mechanical means of carrying out chemical operations on a large scale. This he should learn well, and he should supplement his class-work by learning to express his technical ideas on the drawing-board."

Dr. Lunge concludes as follows:—"I must conclude by stating my conviction, founded upon thirteen and a half years' teaching experience, preceded by sixteen years' manufacturing practice, that in the long run a man who has combined in his studies a really thorough scientific with an appropriate technological training, will have a great advantage both over the pure theorist and over the mere 'practical man.'"

To meet this want a syllabus of lectures and laboratory instruction has been arranged at University College, a college the chemical traditions of which are adorned by the names of Turner, Thomas Graham, Fownes, Williamson, and Charles Graham, all of whom have had the most prominent influence on the development of scientific and industrial chemistry.

THE ELECTROLYSIS OF DISTILLED WATER.

By M. E. DUTER.

The author has employed in his researches distilled water contained in glass tubes with two limbs, which, even after the lapse of several months, did not communicate any alkalinity to the water. The electromotive power employed was considerable, always about 100 volts.

As electrodes were used: (1) an anode and a cathode of platinum; (2) anodes formed of very different metals, chiefly nickel, cobalt, iron, or copper, the cathode being still platinum; (3) an anode of platinum with a cathode of tin, of bismuth, of copper, of lead, of mercury, or of aluminium. In the first case, if the cathode is a fine wire whilst the anode is a broad plate, electrolysis yields for several days nothing but hydrogen. Afterwards oxygen begins to appear at the positive pole, but its volume is always less than half the volume of the hydrogen liberated. Water thus submitted to electrolysis acquires a slightly acid reaction. In the second case the anodes are attacked, and during the first hours of the action they yield monoxides. At the positive pole there appears a jelly which is green with nickel, rose with cobalt, and blue with copper. After some hours the oxides take a darker colour and pass into peroxides. If the electrolysis is let continue for some months the oxide surrounding the positive pole is finally partially reduced. Thus nickelic oxide returned to the nickelous state and became green; cobaltic oxide, which was maroon, became a rose, and that of iron lost its rusty colour and turned almost white. This transformation requires about two months; for ferric oxide it only begins after seven or eight months. It seems as if these deoxidations may be compared with those produced in hydrogen peroxide by oxygenated water. In the third case, where the negative electrode is constituted of a metal other than platinum, this metal, contrary to expectation, is generally oxidised. Tin yields stannic oxide with escape of hydrogen. Bismuth yields similar results. A negative electrode of copper is covered with a deposit which almost stops the passage of the current, even with an electromotive power of 120 volts. Lead at the negative pole is covered with grey tufts, which, if the current is interrupted, give rise to a plumbous oxide, which seems to flow from the electrode like a thin white paste. If the negative electrode is of mercury the free surface of the metal covers itself with asperities of a pasty aspect, which liberate hydrogen and continue so to do for more than an hour after the cessation of the current.

Aluminium is energetically attacked at the negative pole, becoming transformed into alumina. After a time the metal loses its cohesion, splits up, and falls to the bottom of the vessel in the form of fine laminæ and of grey powder.

These experiments, and especially that with aluminium, render it probable that metallic hydrides are formed at the negative pole and are then destroyed by the water with formation of oxide and escape of hydrogen.—*Comptes Rendus* (cix., p. 108).

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

Gem Mining.—During 1887 no work was done either at Mount Mica, Paris, Maine, or at Stony Point, North Carolina, which are the two most noted localities where gems are sought for systematically. At Mount Apatite, Auburn, Maine, some work was carried on during the fall of 1887; 200 dollars worth of tourmalines and 400 dollars worth of other minerals were found.

Several localities in North and South Carolina and Kentucky have been opened and ordinary mining operations carried on for the purpose of producing zircon, and several other comparatively rare minerals which have been only looked upon as gems as heretofore, but are now used for making the oxides of zirconium, lanthanum, cerium, &c. These oxides are needed for manufacturing purposes.

Exceptional Discoveries of Gems—Diamond.—In April, 1887, Mr. Lewis M. Parker, a tenant on the farm of Daniel Light, three-fourths of a mile north-west of Morrow Station, and thirteen miles south of Atlanta, Georgia, found a diamond on the farm. The stone afterwards came into the possession of Mr. W. W. Scott, of Atlanta, who sent it to the writer for examination. It proved to be an octahedral crystal weighing 4 1/8 carats (828 m.grms.), two-fifths of an inch long and one-fourth of an inch wide. It measured 9 by 10 by 7 m.m., is slightly yellow, and has one small black inclusion. The specific gravity was found to be 3·527. Curious long shallow pittings mark the surface. A stone of from 1 1/8 to 2 carats could be cut from it.

Mr. L. O. Stevens, of Atlanta, Georgia, has informed the writer that a coloured man called on him during the past year with a 2-carat diamond, defective and of poor colour, which he stated he had found in his garden within a few miles of Atlanta. He has shown no desire to sell or lend the stone for examination.

Zircon.—Opaque green zircons in crystals 1 inch long and 1½ inches wide, were found by Mr. Nimms in Saint Lawrence county, New York, at the town of Fine. They were curious, but not of gem value. Fully 25 tons of this mineral will be raised during 1888, from Henderson county, Kentucky, for use in a new incandescent gas-burner manufactured in Philadelphia.

Beryl.—Prof. Eugene A. Smith obtained from Coosa county, Alabama, some light golden yellow beryl of sufficient transparency to furnish small gems. Blue-green beryl that afforded fair gems was reported by Mr. William E. Hidden, from Mitchell county, near the Yancey county line, North Carolina.

Phenacite.—Dr. S. L. Penfield describes phenacite from Topaz Butte, 5 miles north of Florrissant and the same distance from Mount Antero, Colorado. Mr. W. B. Smith describes the occurrence of topaz and phenacite at Topaz Butte (*American Journal of Science*, February, 1887, III. Series, vol. xxxiv., p. 130). An extensive find of phenacite crystals (few of gem value, however,) associated with aquamarine crystals, was made at Mount Antero, Colorado, in the fall of 1887. The phenacites were almost quartzoids in form. The occurrence is described by the Rev. R. F. Cross, in a note in the *American Journal of Science*, February, 1887, p. 161, vol. xxxiv.

Garnet.—A variety of spessartite garnet was found at Amelia Court House, Virginia, in masses several inches across, and dark brown, dark red, or honey-brown in colour, which would afford cut gems from 1 to 10 carats in weight. These are the finest specimens of this variety of garnet yet found. Fully 1½ tons of the almandite garnets of Salida, Colorado, were found during the past year and sold as tourists' or mineralogical specimens at from 30 cents to 1 dollar a pound. One absolutely perfect dodecahedron weighed over 14 pounds. In the *Proceedings of the Philadelphia Academy of Natural Sciences*, 1886, p. 355, Dr. George Koenig describes a titaniferous garnet from south-western Colorado, and also analysis of schorlomite from Magnet Cove, Arkansas, which he finds to be titaniferous garnet.

Tourmaline.—A large number of green tourmalines, some quite stout and several inches in length, have been found at Franklin Furnace, Sussex county, New Jersey, but although they are an important addition to our mineralogical collections, and the outer parts of some of the crystals are of a rich almost chrome green, yet not a single one was observed which would cut a transparent gem of even a few carats.

Prof. R. B. Riggs, of the laboratory of the Geological Survey, recently made over 25 analyses of tourmalines of all colours. He found the question of the colour of the lithia tourmaline a very interesting one. The colour of the iron and magnesian varieties depends on the amount of iron present. It ranges from the colourless De Kalb through all the shades of brown to the Pierrepoint black, whilst the lithia tourmaline, containing more or less manganese, gives the red, green, and blue, as well as the colourless varieties. The shades of colour do not depend on the absolute amount of manganese present, but rather on the ratios existing between that element and iron. Thus, when the amount of manganese bears a specific proportion to the iron, we have the colourless pink or very pale green tourmaline. An excess of manganese produces the red varieties; and if the iron is in excess the various shades of green and blue result.

Rubellite.—Mr. William Irelan, jun., reports the finding of transparent rubellite in fine crystals 1 to 2 inches long, in San Diego county, California.

Hiddenite.—Rev. Alfred Free, in a report on a placer mine at Bracket Town, McDowell County, North Carolina, mentions the finding of a small crystal of spodumene of the hiddenite variety. He had also observed blue, green, and pink tourmaline at the same locality.

Rock Crystal.—In the last report reference was made to the occurrence of rock crystal in what was believed to be a part of Virginia, but which, on visiting the locality, the writer found was merely the mountainous part of Ashe county, North Carolina. My attention was first called to this locality by the receipt thence, by Messrs. Tiffany and Co., of a 51-pound fragment of a large crystal, which was said to have been broken from a mass weighing 300 pounds by a twelve-year old mountain girl. This large crystal was found on the Mintor Blevin Farm, on Long Shoal Creek, in Chestnut Hill township, though crystals have also been found at two places 600 feet apart on the L. C. Gentry farm, about one mile from the former locality. All three places are 50 miles from Abingdon, Virginia, and 40 miles from Marion, Virginia. Crystals have also been found close to the north fork of Piny Creek, on the Saint Ledger Brooks Farm. At the latter place was found a remarkably clear distorted crystal, weighing 20½ pounds, which is absolutely perfect, and is the finest piece of rock crystal ever found in the United States; and on the Gentry Farm one crystal was found weighing 188 pounds and another weighing 285 pounds. The latter was 29 inches long, 18 inches wide, and 13 inches thick, showing one pyramidal termination entirely perfect and another partly so; it sold for over 500 dollars for use in the arts. A number of others have also been found. All these localities are on a spur of Phœnix Mountain, and the crystals have all been found in decomposed crystalline rocks, principally coarse felspathic granite, which has all decomposed, even to a greater depth than that at which these crystals occur. Most of them are obtained by digging where one crystal has been found, or by striking and unearthing them with a plough. Altogether several dozen crystals have been found, weighing from 20 to 300 pounds each, and future working will doubtless bring many fine ones to light. Some of these afford larger masses of clear rock crystal

* Abstract from "Mineral Resources of the United States."

than have ever before been found in the United States, and suggest its use for such objects of luxury as crystal balls, clock cases, mirrors, &c., which are now to be seen in the Austrian treasury at Vienna.

From the vicinity of Fairfax county, Virginia, Mr. James W. Beath obtained quartz with alternate green and white veinings, the green being produced by chloritic inclusions. When cut it forms an interesting ornamental stone, and several hundred dollars' worth of it have been sold.

Mr. H. L. Hosmer reports that crystals of smoky quartz a foot in length are occasionally found at Sterling, Montana.

Chrysoprase.—Mr. William Irelan, jun., reports from Tulare county, California, beautiful semi-transparent chrysoprase of fine colour. This has also been found in Douglas county, Oregon.

Agate.—At Sioux Falls, Dakota, the company that is cutting and polishing the agatised wood from Arizona and the quartzite found at Sioux Falls has, after a great deal of experimenting, perfected the methods of sawing and polishing hard materials so as greatly to reduce the cost. Among the objects produced were a round column 11½ inches wide and 21 inches high, cut transversely across the tree so that the heart was visible on two sides of it, with the radiations in all directions; and sections measuring 25, 24, 17½, and 13 inches in diameter, respectively, so highly polished that when turned with the back to the light they form a perfect mirror. All the specimens were brilliant in colour and rivalled any work ever done in hard materials. The company has removed from the forest 180 tons of material, and 20 tons of sections have been ground down to show its characteristic beauties. Perhaps 100,000 dollars worth is now undergoing the cutting and polishing process.

Pectolite.—A massive pectolite of unusually dense structure has been announced by Mr. William P. Blake as occurring in Tehama county, California, in masses of considerable size and susceptible of a high polish. In a letter to the writer he gives the following description:—"It occurs in a vein, and is broken out in rough tabular masses from 2 to 3 or more inches in thickness, but it is reported that much larger masses can be obtained. It is exceedingly tough and hard to break. The punctured surfaces are irregular, without cleavage, but have a silky lustre and crypto-crystalline structure, exhibited in extremely fine inseparable fibres, which are radial, curved, and interlaced, and are perhaps embedded in a siliceous magma, but the fibres constitute the bulk of the mass. the colour is white, with a delicate shade of sea green, and translucent. Exposed or weathered portions lose their-porcelain like translucency, and become white and somewhat earthy in appearance, and exhibit the crypto-fibrous structure with more distinctness. Specimens cut and polished across the end of a slab-like mass show on one side a narrow selvage of breccia, made up of fragments of the pectolite and of dark coloured wall rock mixed and firmly cemented together. On the opposite side or border of the mass there are distinctly formed parallel planes of concentric layering, from the surfaces of which the fibres diverge. These layers and the brecciated border opposite show the vein-like formation of the mass between the walls. The hardness is 6 to 6·5. In the blowpipe flame it burns to a white enamel and gives off a little water. It may be found useful as an ornamental stone for making small objects—cups, plates, handles, or for carving figures, or inlaid work." This is identical with the pectolite from Alaska, described by Prof. F. W. Clarke.

Peristerite.—Large quantities of peristerite are reported by Mr. C. M. Skinner at Cavendish, Vermont, near Cavendish Falls, in the railroad cut, 22 miles north-west of Bellows Falls.

Oligoclase.—Of great interest is the transparent oily green oligoclase containing small, white, star-like inclusions, which impart to the mass all the appearance of green glass, and with included white minerals found at a depth of 400 feet in mica near Bakersville, North Carolina. It was found by Mr. Daniel Bowman.

A very interesting variety of sunstone was found by Mr. J. A. D. Stephenson at the quarry in Statesville, North Carolina. Several hundred dollars' worth of it has been sold as gems.

Albite.—In the Allen mica mines at Amelia Court House, Amelia county, Virginia, as a by-product in mica mining, a remarkable series of albite has been found, tabular, but measuring 4 to 7 inches in length and forming large groups; also the same mineral in massive form of the moonstone variety, and tons of amazonstone in bright cleavages.

Rhodonite of the variety known as fowlerite has been found in Franklin Furnace, New Jersey, in groups of rich, flesh-coloured crystals finer than ever before known. Some of these were 6 or 7 inches in length and several inches thick, forming groups a foot across. Although of value for gem material, they possess a higher mineralogical value, and more than 1000 dollars' worth was sold for specimens. The rhodonite so well known as occurring in boulders at Cunningham, Massachusetts, has recently been traced to the ledge, and we may now hope to see this stone used extensively for decorative and ornamental purposes, as at this locality it is one of the richest pink and flesh-coloured minerals known.

Turquois.—Additional evidence of the antiquity of the turquois workings of New Mexico and Arizona has been gathered by the Hemenway expedition, sent out by Mrs. Hemenway under the direction of Mr. Frank H. Cushing. About ten miles from Tempe, Arizona, where the excavations are being made, a shell encrusted with turquois and garnet representing the form of a frog was found.

Cyanite.—Mr. Daniel A. Bowman communicates that the cyanite mentioned in the last report was found near the summit of Yellow mountain, alongside the road to Marion, about 4 miles south-east of Bakersville, North Carolina, at an altitude of 5500 feet. Some of this is transparent, from one-eighth to one-half inch across, and several inches long. So rich is its colour that it was sold for sapphire. Its low hardness unfits it to some extent for use as the gem for which it is to be worn. It is a handsome mineralogical gem, however.

Crocidolite.—In the *American Journal of Science*, III., vol. xxxiv., p. 108, Prof. A. A. Chester published analyses of the crocidolite from Beacon Hill Pole, Cumberland, Rhode Island, an interesting occurrence of this mineral, though not in gem form.

Labradorite.—The well-known Labradorite rock in Lewis county, New York, is so plentiful that the reflection of the boulders has given the river that runs through the locality the name of Opalescent River. This is being extensively cut as an ornamental stone.

Mexican Onyx.—The handsomest and lowest priced of our ornamental stones, and one which has been introduced most extensively, is the so-called Mexican onyx or Tecalli, as it was first called, from the town of that name in the state of Pueblo, Mexico, where it is found. The deep colours are richer than those of any marble known, and its wavy stalagmitic structure and the high polish which it can take have made it popular throughout the whole civilised world. With a metal mounting the effect is greatly enhanced. It occurs in almost unlimited quantities, and fully 500,000 dollars worth has been used in the United States for table tops, mantels, vases, &c.

(To be continued).

Occurrence of Ferrous Oxide in Potassium Sulphocyanide.—J. Kranzfeld (*Pharm. Zeitung für Russland*).—Such sulphocyanide turns red on exposure to air, and is of no use for the detection of iron. It may easily be purified by solution in aqueous alcohol, addition of a ew drops of ammonium sulphide, and filtration.

NOTICES OF BOOKS.

Scientific and Industrial History of Aniline Black (Histoire Scientifique et Industrielle du Noir d'Aniline). By E. Noelting, Director of the School of Chemistry, at Mulhouse. Mulhouse: Strickelberger.

This work opens with a very elaborate history of aniline black, in which the name of Lightfoot is not once mentioned. We find accounts of experiments and observations made both in the laboratory and in industrial establishments, some before and some subsequent to Lightfoot's invention. But the former led to no definite and tangible results, and the latter, save the discovery of the remarkable action of the vanadium salts, have been more curious than useful.

In the second chapter the industrial applications are brought forward. After speaking of the use of aniline blacks in powder, the author passes to the formation of blacks upon the fibre. Here, at last, we find a notice of Lightfoot. It is said that he "introduced into the production of aniline black an improvement such that he is generally considered as its originator"—a view which M. Noelting by no means seems to share. But the real motive of the book is made to appear in the preface. The author writes:—"In many countries the application of aniline black is entirely free; in France the patents of M. Grawitz claim the monopoly of this industry, and have led to much litigation. It seems to us important to submit the patents of M. Grawitz to a thorough discussion."

This, of course, is a very delicate matter. We are not sure how far the discussion, even of foreign patents, with reference to their validity, is safe in England. Hence, pending the necessary restriction of English libel law, we shall not express any opinion on the matter at issue.

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—In Chem. News, vol. lx., p. 36, I noticed a letter from your correspondent, Thos. T. P. Warren, on thiocamf, now being used as a disinfectant, and stating that the preparation, a solution of camphor in sulphurous acid, was the invention of Alexander Parkes, and patented by him, No. 11,147, 1846, as a solvent of indiarubber.

As the inventor of the cold converting process of vulcanisation, I wish to say that, although in my specification nothing was said of this peculiar property of the camphor solution, I was well aware of the fact, as both camphor and sulphurous acid separately are disinfectants, and a friend of mine wished to join me in bringing it out for this purpose. Being, however, much engaged at that time with other important matters, I could not go into it, and it passed from my memory. Still the original idea was my own, and my only object in troubling you with this letter is to point this out to your readers.—I am, &c.,

Alexr. Parkes.

Chancellor Rd., Dulwich,
August 1, 1889.

Detection of Jute in Linen or Hempen Tissues.—The warp, which generally contains the jute, is freed from the weft and dipped in the solution of an aniline salt. Linen and hemp remain unchanged, whilst raw jute is stained an intense yellow. To test for bleached jute the thread is plunged into a solution of chloride of lime, drawn out, taken through hydrochloric acid, washed, and touched with ammonia. The presence of jute is shown by a characteristic violet-red colour, whilst linen and hemp turn brown.—*L'Industrie Textile* and *Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 4, July 22, 1889.

On Zinc and Cadmium Chromites.—G. Viard.—The author obtains these compounds by a modification of Gerber's process. He causes the vapours of the chlorides, carried along by a slow current of nitrogen or carbon dioxide, to act upon neutral potassium chromate. Both the chromate and the chloride are placed in boats in a porcelain tube. The zinc chromite forms black regular octahedral crystals, hard enough to scratch quartz and not attacked by acids. The cadmium compound is formed by a similar process, and yields crystals which scratch glass, but not quartz.

Formation of Crystalline, Alkaline, and Alkaline-Earthy Platinates at High Temperatures.—G. Rousseau.—The author has observed the rapid corrosion of platinum crucibles by basic fluxes. The products obtained were often mixed with metallic platinum; sometimes, also, when the fluxes were very alkaline, the crystals collected contained considerable quantities of platinic oxide united to cobalt, iron, and aluminium oxides. This unexpected formation of alkaline and alkaline-earthy platinates was observed between 800° and 1300°. The author has studied the barium and sodium platinates, which represent two very distinct types. In stability the platinates are comparable to the manganites and the ferrites. They present a new instance of the formation of a compound at temperatures higher than the point of their decomposition.

On the Ammonio-cobaltic Tungstates and Vanadates.—Ad. Carnot.—This paper will be inserted in full.

On Diethyl-amido-α-propionic Acid.—E. Duvillier.—This compound is obtained at a temperature of 100° by the reaction of 1 mol. of α-bromo-propionic acid upon about 3 mols. of aqueous diethylamine. The acid is very soluble in alcohol and in water, which it attracts as eagerly as does calcium chloride.

The Application of the Measure of Rotatory Power to the Study of the Compounds Resulting from the Action of Malic Acid and Ammonium Molybdate.—D. Gernez.—The progressive addition of ammonium molybdate to a solution of malic acid determines an increase of rotation, the initial value of which, 0·12, gradually reaches a maximum value of −5·19, or 35 times the rotation of the malic acid contained in the solution. This maximum corresponds to a combination of 9 equivs. of malic acid to 1 of ammonium molybdate. As this salt contains 3 equivs. of ammonia, the compound contains 3 equivs. of base to 1 of acid. For weights of the molybdate greater than one-ninth of the equivalent the rotation retrogrades, passing from left to right, and augments progressively. An abrupt variation in this increase sets in when the liquid contains 3 equivs. of acid to 1 of the salt. An attentive examination of the progress of the phenomena shows that at the outset very slight quantities of the molybdate produce considerable effects; thus, 1-384th equivalent of ammonium molybdate doubles the rotation presented by the active liquid.

Detection and Determination of Sodium Hydrocarbonate in Milk.—L. Padé.—This paper will be inserted in full.

Improvements Introduced in the Preparation of Crystalline Hæmoglobine by Hoppe-Seyler's Process: New Method for Preparing this Body.—M. Mayet.—This memoir will be inserted at some length, if possible.

Moniteur Scientifique, Quesneville.
4th Series, Vol. iii., May, 1889.

On the Theory of Dyeing and on the Causes of the Spots Observed on Dyeing Cloth.—Dr. Paul Julius.—Among the products of the decomposition of wool under the influence of water, alkalies, and acids there are compounds soluble in water and others which are insoluble, and which are able to precipitate many colours and mordants from their solutions in the form of insoluble lakes. The inequalities often observed in dyeing woollen cloth are due to the presence of such products.

Formation of Saccharic Acid as a Characteristic Reaction of Dextrose.—R. Gans and B. Tollens.—From *Liebig's Annalen.*

A Novel Alkaloid: "Imperialine."—M. Fragner (*Berichte*).—This alkaloid, $C_{35}H_{60}NO_4$, is obtained from the bulbs of the fritillary. Its characteristic reactions are:—Strong sulphuric acid turns imperialine a pale yellow; if ground up with sugar and moistened with sulphuric acid it turns first a yellowish green, then a light brown, a flesh colour, a cherry-red, and lastly a dark dirty violet. With Trōhde's reagent it takes a light yellowish green; with Mandelin's reagent an olive green, then a reddish brown, and lastly a dark brown.

Manufacture and Purification of Carbon Disulphide.—Ignatius Singer.—From the *Journal of the Society of Chemical Society.*

On Yorkshire Grease.—G. H. Hurst.—From the *Journal of the Society of Chemical Industry.*

Rapid Analysis of Prussian Greens.—A. Chenevier.—Prussian green is a pigment much used in paint and varnish. It is a mixture of chrome yellow and prussian blue let down with lead and calcium sulphates, ochre, china clay, &c. The colour is ground up in water acidulated with hydrochloric acid and placed in a stoppered flask. Potassium iodide is added in slight excess. It is digested, starch paste is added, and it is titrated with decinormal sodium thiosulphate. In presence of prussian blue it is impossible to catch the end of the operation. Therefore, for a speedy and approximate determination after the addition of each c.c. of the thiosulphate, a drop of the liquid is placed upon a plate of copper. As long as this liquid contains free iodine it leaves upon the plate a white spot of copper iodide. As soon as the thiosulphate is in excess no spot is produced. If more time is available the following modification of the process may be used:—2·16 grms. of the green well ground up in a glass mortar with a little water and 2 to 3 c.c. of hydrochloric acid (sp. gr., 1·18) are placed in a graduated and stoppered jar of 200 c.c.; 3 to 4 grms. of potassium iodide are added and the whole is let digest for fifteen minutes. The jar is filled up to 200 c.c. with water, mixed, and let let settle for two hours. At the end of this time 100 c.c. of the clear liquid, corresponding to 1·08 of the green, are drawn off with a syphon. In this liquid the free iodine is determined with decinormal thiosulphate, using starch-paste as indicator. Each c.c. represents 1 per cent of lead chromate. The process is accurate to 0·2 or 0·3 per cent. *Determination of the Prussian Blue.*—To 4 grms. of the green ground up with 10 c.c. of water and 5 c.c. of hydrochloric acid are added 3 to 4 grms. of ferrous sulphate dissolved in 20 c.c. of water to reduce the lead chromate. After digesting from five to ten minutes an excess of soda-lye is carefully added, which precipitates the oxides of iron and decomposes the blue. It is poured into a flask marked at 200 c.c. and heated almost to a boil. When cold the volume is made up to 200 c.c. After settling, 100 c.c. of the clear liquid (corresponding to 2 grms. of the green) are drawn off, and, after acidulation with sulphuric acid, titrated with permanganate.

Method for Removing Nitrogen Compounds from the Sulphuric Acid used in Kjeldahl's Process.—G. Lunge (*Zeits. f. Angewandte Chemie*).—The author criticises the method of Meldola and Moritz, who propose to add a small quantity of sodium nitrite and heat strongly.

Determination of Nitrogen. Methods Officially Adopted by the Congress of American Agricultural Chemists.—Already noticed.

Determination of Phosphoric Acid Adopted as Above.—Already noticed.

New Methods of the Elementary Analysis of Organic Substances in the Moist Way.—J. Messinger (*Berichte* and *Chemiker Zeitung*).—The author finds that all organic substances, if heated in an undiluted sulphuric solution with chromic acid, undergo a complete combustion. The carbon is liberated as carbon dioxide; nitrogen escapes as such, or as ammonia. The sulphur, phosphorus, and arsenic remain as sulphuric, phosphoric, aud arsenic acid. The halogens are set at liberty.

Convenient Method for Preparing Oxygen.—C. F. Gœhring (*Chemiker Zeitung*).—The author uses oxygenated water as material.

Determination of Paraffin.—B. Pawlewski and J. Filemonowicz.—Already noticed.

Employment of Diazo-compounds for Detecting Organic Substances in Water.—P. Griess (*Berichte*).—Already noticed.

Composition of Gums and Resins.—Williams.—From the Chemical News and *Chemiker Zeitung.*

Determination of the Higher Alcohols, especially of Amylic Alcohol, in Brandies and Industrial Alcohols (*Chemische Industrie*).—Already noticed.

On Dextro-rotatory Honey.—Dr. E. O. von Lippmann.—The author notices the presence of saccharose in honeys obtained from hives situate near sugar refineries. Such honey is deficient in aroma.

Assay of Peppers.—J. N. Zeitler (*Zeitschrift f. Angewandte Chemie*).—Already noticed.

Artificial Coffee.—A notice of fraudulent coffee beans moulded in a machine, for which a patent has been actually granted in Germany.

Historical Account of the Development of the Textile Industry.—Dr. O. N. Witt.—A translation of an entire work and not admitting of useful abstraction.

The Favier Explosives.—A reply to a memoir of German origin, unfavourable to the Favier explosive.

Industrial Review and Patents.—Abridged specifications of a number of chemical patents, chiefly of German origin.

Volumetric Determination of Stannous Compounds.—Adolf Jolles (*Chemiker Zeitung*).—The author adds to a known volume of a solution of alkaline manganate of known strength the solution of stannous salt to be determined, with frequent agitation until the green colour passes into a yellowish brown. The solution of manganate is made by dissolving in a beaker 4 to 5 grms. potassium manganate and 8 to 10 grms. potassium hydroxide in water, transferring the clear solution cautiously into a litre flask and filling up to the mark. For standardising, exactly 5 or 10 c.c. of the manganate solution are run into an Erlenmeyer flask and a solution of tartar-emetic (10 grms. of the pure salt per litre) is added, with frequent agitation, until the green colour turns to a yellowish brown. For standardising the stannous salts from 0·2 to 0·4 grm. of the salt in question, or of tin, is dissolved in hydrochloric acid in a current of carbonic acid; the clear solution thus obtained is poured into a 250 c.c. flask and filled up to the mark. Exactly 5 or 10 c.c. of the standardised manganate solution are dropped from a burette into a small Erlenmeyer flask and the stannous chloride solution is added, likewise from a burette, with frequent agitation, untill the yellowish brown colour appears.

MISCELLANEOUS.

Cooking by Electricity.—The Hotel Bernina, at Samaden, has for some time been lighted with electricity, power being supplied by a waterfall. As during the day this power is not required for lighting, and is therefore running to waste, the proprietor of the hotel has hit upon the idea of utilising the current for cooking when it is not required for lighting, and an experimental cooking apparatus has been constructed. This contains German silver resistance coils, which are brought to a red heat by the current, and it has been found possible to perform all the ordinary cooking operations in a range fitted with a series of such coils.—*Engineering and Mining Journal.*

Remarks on the Physiology of Tannin. — F. Reinitzer.—The author protests against the present universal custom of giving the name "tannin" or "tannic acid" to all vegetable compounds which give with ferric chloride blue or green colourations or precipitates, and which are precipitated by solution of gelatin. As regards the former reaction he points out that ferric chloride colours aqueous solutions of mono- or polyvalent phenols blue, green, or violet. Hence he considers it very probable that the tannins contain hydroxyl-groups with a phenolic character. He further reminds us that many tannins do not precipitate solutions of gelatin at all, others occasion merely a turbidity, and others again produce a very imperfect precipitation. He doubts whether all these bodies can fulfil the same physiological function, and considers the idea of "tannin" about equal in value to that of "bitter principle," under which substances of very different character were formerly included. — *Deutsch. Botan. Berichte* and *Chemiker Zeitung.*

Poisoning by Cotton Dyed with Lead Chromate.—Th. Weyl.—Dr. Carry, of Lyon, reports on a series of poisoning cases among women engaged in winding yellow or orange yarns. All the symptoms indicated lead-poisoning. Prof. Pouchot, of Lyon, however, found in three samples submitted to his examination no lead, and stated that the yarns were mordanted with a salt of antimony and dyed —No. 1 with Martius' yellow, No. 2 with Jaune solide, and No. 3 with "Jaune N Poirrier." The writer obtained, at the request of Dr. Carry, specimens of the suspected yarns, and found, in concert with G. Schulz, of Berlin, that they were dyed with lead chromate, and not with the dyes above mentioned. Both the lead and the chrome were not merely qualitatively recognised, but quantitatively determined. How Prof. Pouchot can have been deceived is questionable. The use of lead chromate is legal both in France and Germany. In an appendix the author mentions that he found in a saddler's workshop in Berlin sewing thread dyed orange with lead chromate. It could scarcely be doubted that lead poisoning might ensue from the continued use of such thread.—*Zeit. f. Hygiene* and *Chemiker Zeitung.*

Determination of Nitrogen and of Phosphoric Acid in Organic Bodies.—Dr. Otto Lange (*Chemiker Zeitung*).—The author finds that the liquid obtained by the sulphuric treatment of the sample in Kjeldahl's process may be employed in determining the total phosphoric acid. He uses for the attack a flask of 300 to 350 c.c. capacity. He treats 10 grms. of the substance with 50 c.c. of undiluted sulphuric acid and 0·5 grm. of mercury or 0·5 to 1 grm. of copper sulphate. The liquid, after the action is over, is diluted with water to 500 c.c. and an aliquot part is used for the determination of the ammonia formed. Another portion, say 50 c.c. (corresponding to 1 grm. of the substance), is treated with 100 c.c. of Maercker's liquor and 25 c.c. of magnesia mixture. The whole is stirred until the appearance of the precipitate, which may be filtered after fifteen minutes. Maercker employs citric acid 1½ kilos., water 3 litres, ammonia at 24 per cent 5 litres, and adds 7 litres more water.

Modification in the Process of Organic Analysis by Combustion.— W. L. Dudley (*Berichte* and *Chemiker Zeitung*).—The author effects the combustion in a platinum tube of 48½ c.m. in length and 1½ c.m. in diameter, extended at one end by a tube of the same material 13 c.m. in length and ½ c.m. in diameter. The other extremity, serving for the introduction of the substance and the entrance of the gases—air, oxygen, or nitrogen, as the case may be,—is closed by a screw stopper traversed by a tube ½ c.m. in diameter. The arrangement and the progress of the analysis are those usual in combustions with a fixed tube. Behind the boat containing the substance the author places a coil of fine platinum wire gauze, which is easily removed when it is necessary to insert or withdraw the boat. This coil occupies 3½ c.m. in length and serves to burn the vapours.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that JULIUS MARX, of Ulm a/Donau, Wurtemburg, in the Empire of Germany, has applied for leave to amend the Specification of Letters Patent No. 2367 of 1888 for "Improvements in the method of and means for separating matters in solution by osmose, dialysis or diffusion, or by electrolysis, or by a combinaton of those processes."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 31st July, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
Comptroller-General.

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THE CHEMICAL NEWS.

VOL. LX. No. 1551.

NOTES ON THE ABSORPTION-SPECTRA OF OXYGEN AND SOME OF ITS COMPOUNDS.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.

THE absorption-spectrum of oxygen has engaged attention not only on account of the important part which that element plays in the world, but because of the remarkable character of that absorption, so strongly marked, exhibiting bands of two essentially different classes, and extremely variable under varying circumstances of condensation and combination.

It may be expected that the study of it will reveal something new as to the nature of the molecular changes brought about by different circumstances, physical and chemical.

We have already published notes of some of our experiments on this subject (*Phil. Mag.*, September, 1888), and these confirm generally the observations of Egoroff, Janssen, and Olszewski.

A diagram accompanying the paper represents the absorption of 18 metres of ordinary oxygen gas at a pressure of about 97 atmospheres, that is, of a mass of oxygen rather greater than is contained in a vertical column of equal section of the earth's atmosphere. Under the circumstances of the experiment the absorptions A and B are very black, and the lines of which they are composed appear much broader than in the ordinary solar spectrum. The other bands are all diffuse at their edges, and, so far as we have observed, unresolvable into lines. It will be noted that the complete absorption of the ultra-violet rays does not extend quite so far down as the limit of the solar spectrum, though it approaches that limit. There is a diffuse edge of gradually diminishing absorption succeeding the complete absorption, and this fact, together with the rapid diminution of the extent of the complete absorption with decrease of pressure, lead us to class this absorption of the extreme rays with the diffuse bands, which, according to Janssen, increase in intensity as the square of the density of the gas. If that be so, it is unlikely that the limit of the solar spectrum is due to the absorption of ordinary oxygen. For though we may suppose interplanetary space to be pervaded by materials similar to our atmosphere, yet they must be in such a state of tenuity that, although they may to some extent reinforce A and B, they will not add sensibly to the strength of the diffuse bands. Moreover, these bands, though identical in position, so far as the blue and less refrangible part of the spectrum is concerned, with bands observed by Brewster and others in the solar spectrum, are seen much more strongly through our tubes of compressed oxygen than they appear in the solar spectrum with a low sun. The ultra-violet bands, of which the one near N appears in our photographs nearly as strong as the band just above F, and that in the indigo, have not, so far as we are aware, been noticed in the solar spectrum. Probably they would appear if photographs were taken with small dispersion when the sun was low.

As the pressure in the tube diminished, the bands rapidly faded; that in the indigo, with an oscillation-frequency or wave-number about 2240, was the first to disappear, then those near L and O and that near E. At the same time the limit of the transmitted ultra-violet light advanced from an oscillation-frequency of about 3575 at 97 atmospheres, to 3710 at 50 atmospheres, and 3848 at 23 atmospheres. At 20 atmospheres the three bands above C, D, and F, respectively, were still visible, though faint. B remained visible until the pressure was reduced to 2 atmospheres, and A could still be seen, but with difficulty, when the pressure of the 18 metres of oxygen was reduced to 1 atmosphere.

When atmospheric air was substituted for oxygen we found that 7 atmospheres was the limit of pressure at which we could certainly distinguish A, and 18 atmospheres the limit at which we could see B. It is a difficult matter to say exactly when an absorption becomes invisible, but the observations on air were made under the same circumstances as those on oxygen, and the two sets of observations were fairly comparable. With air at 75 atmospheres the three bands above C, D, and F, respectively, could all be seen, but that near C only with difficulty. The mass of oxygen and its *partial* pressure in the tube was in this case less by about one quarter than that which was required to bring out the bands when oxygen alone was used. The cause of this may be that the development of the diffuse bands depends in some degree on the total pressure of the air, and not only on the partial pressure of the oxygen in it.

The mass of oxygen which when unmixed with nitrogen made A visible would correspond to that in the tube filled with air at 5 atmospheres, and that which made B visible would correspond to air at 10 atmospheres. The differences between these pressures and those which are actually needed to render A and B visible seem too great to be ascribed to errors of observation, and seem to indicate that the addition of the nitrogen has some effect on the absorptive action of the oxygen. On the other hand, Egoroff found that he could still distinguish A when the thickness of air at ordinary pressure was reduced to 80 metres (*Compt. Rend.*, vol. ci., p. 1144). This amount of air corresponds to rather less oxygen than our tube would hold at a pressure of 1 atmosphere. Differences in the sources of light, in the spectroscope, and the observers, would, however, count for a good deal in observations of this kind.

In order to try the influence of temperature on the absorption, the shorter of our experimental tubes, 165 c.m. long, was surrounded by a jacket filled with a mixture of solid carbonic anhydride and ether, which was rapidly evaporated by means of a large air-pump. By this means the temperature would be reduced to $-100°$. The absorption of oxygen at several different pressures up to 104 atmospheres was observed through the cooled tube. We were not, however, able to detect any increase of intensity or other change in the absorptions which could be ascribed to the cooling. To try the effect of an increase of temperature the 18-metre tube was surrounded by a jacket and heated up to 100° by steam. Heating appeared to render the diffuse bands rather more diffuse and less distinct. On the whole the influence of a change of temperature of 100° either way is slight.

We have observed repeatedly the absorption of liquid oxygen in thicknesses of 8 and 12 m.m. Our observations confirm those of Olszewski. 8 m.m. of liquid oxygen gives plainly the three diffuse bands above C, D, and F, respectively. With a thickness of 12 m.m. we were not able to detect any more.

We observed the absorption produced by liquid oxygen on the one hand when it was cooled by its own evaporation until the tension of its vapour was only equal to that of the atmosphere, that is, to a temperature of $-181°$ according to Olszewski, and also when the temperature of the liquid was allowed to rise under pressure up to nearly the critical temperature. There appeared to be no appreciable difference in the absorption under these different circumstances when the oxygen was completely liquid, when it was near its critical temperature, and when it was completely gaseous; so far at least as concerns the three principal bands, which were all that could

* A Paper read before the Royal Society, June 20, 1889.

be seen in the light transmitted by the liquid in a thickness of 12 m.m.

It will be observed that taking the density of oxygen at $-181{\cdot}4°$ to be 1·124, as given by Olszewski, 12 m.m. of the liquid would be equivalent to 9·37 metres of the gas at atmospheric pressure — hardly more than half the thickness required to make A visible. The experiments, therefore, point to the conclusion that gaseous and liquid oxygen have the same absorption-spectrum. This is a very noteworthy conclusion. For, considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen, the persistency of the absorptions of oxygen through the stages of condensation to the state of complete liquidity implies a persistency of molecular constitution which we should hardly have expected.

In order to compare the absorption of ozone with that of oxygen we employed a tube 12 feet long, made of tin-plate fitted with glass ends and coated with paraffin on the inside. We could not use the 18 m. steel tube on account of the action of the ozone on the metal, which rapidly reduced the proportion of ozone, and also because we could not conveniently cool it. Ozonised oxygen was passed into the tin tube for some time, while the ozoniser and the tube itself were cooled with ice and salt. The lime-light, viewed through the tube, looked very blue, and also the spot of light thrown from the tube on to a sheet of white paper was equally blue, indicating a considerable absorption of the less refrangible part of the spectrum. The absorption, so far as the visible rays are concerned, appeared to be of a general character, for the spectroscope revealed only four extremely faint absorption-bands. The centres of these bands were at about the wave-numbers 1662, 1752, 1880, and 1990, and their positions with reference to the bands of oxygen are indicated in the diagram. They were so faint as to be seen only with difficulty. When the hot carbon of an arc lamp was substituted for the lime-light they were rather more distinct, but the positions of the edges were undefinable. The light of a gas-lamp was insufficient to show them, and they were no better seen with a single-prism spectroscope of low dispersive power than with the spectroscope we employed for observing the oxygen. Only one of these bands, as shown by the diagram, is nearly coincident with an oxygen-band, namely, that near E, the faintest of the oxygen-bands. That at wave-number 1752 overlaps the strongest oxygen-band, but not at its strongest part, and has none of the peculiar character of its shading, abruptly increasing on the less refrangible side and slowly decreasing on the other side. Photographs of the spectrum (taken through a tube with quartz ends) showed that the ozone absorbed all the rays above the wave-number 3086—a point between Q and R—while partial absorption extended below Q. We may say, therefore, that we can trace no identity between the absorptions of ozone and those of ordinary oxygen. There is no mere displacement of the bands, such as we sometimes get when a coloured substance is dissolved in different menstrua, nor any such a resemblance as we have between the absorption-bands of the different cobaltous salts derived from different acids.

The four bands which we see to be produced by ozonised oxygen correspond fairly with the 2nd, 3rd, 5th, and 6th of the bands described by Chappuis as due to ozone (*Annales de l'Ecole Normale*, 2nd ser., vol. xi., May, 1882). These four bands, he says, are the first to be seen. We have failed to perceive any others with the 3·66 m. tube, though the oxygen was highly ozonised and maintained at at a low temperature. None of the bands were of sufficient intensity to make themselves visible on our photographic plates.

It will be noted that the absorption by ozone extends far below the limit of the solar spectrum. We found, however, that by diminishing the proportion of ozone to oxygen in the tube the limit of the transmitted light was continually advanced, as already described by Hartley. The limit of the solar spectrum may, therefore, very wel be determined by the average amount of ozone in the atmosphere, as Hartley supposes. The known variations in the limit of the solar spectrum may be taken as confirmatory of this hypothesis, although the comparatively small amount of these variations is certainly less than we should have expected if they measure the changes in the proportion of ozone in the atmosphere.

The absorptions of the class to which A and B belong must be those which are most easily assumed by the diatomic molecules (O_2) of ordinary oxygen. Whether oxygen in more complex molecules, as in ozone (O_3), may be capable of taking up the corresponding vibrations cannot easily be determined, because we cannot isolate ozone; but since none of the compounds of oxygen with nitrogen, hydrogen, or carbon, or, so far as known, with any other element, exhibit these absorptions, it is very probable that they are peculiar to the molecule O_2. From this point of view it will be interesting to determine—as we hope to do shortly—whether liquefied oxygen, which we suppose to have more complex molecules, produces these absorptions. The corresponding spectrum of emission has not as yet been observed, probably because the agency employed to render the gas luminous breaks up the molecules into single atoms of oxygen.

As for the other class of absorption, the diffuse bands, since they appear to have intensities proportional to the square of the density of the gas, they must depend on a change produced by compression. This may either be the formation of more complex molecules, as for example O_4, corresponding to the deviation from Boyle's law exhibited by oxygen gas, or it may be the constraint to which the molecules are subject during their encounters with one another. Increase of temperature would affect the former, tending to diminish the number of complex molecules formed at a given pressure, but would have no effect on the latter, for though the number of encounters of the molecules in a given interval of time would be greater the higher the temperature, yet so long as the volume was unaltered the ratio of the duration of an encounter to that of free motion would be sensibly unaltered. So far as any change due to temperature has been observed, it is that a rise of temperature slightly weakens the diffuse absorptions.

Reverting to the compounds of oxygen, none of them show the absorptions of oxygen, not even the general absorption of the ultra-violet rays. Some of them, such as water and carbon dioxide, appear quite transparent to ultra-violet rays, while in others, such as nitrous oxide, which show a general absorption of the ultra-violet rays, the limit of transparency is different from that of oxygen. In other respects we may say that there is no resemblance between the absorptions of the compounds of oxygen and those due to oxygen itself. Some of the former have very definite and characteristic absorptions, such as the well-known spectra of the peroxides of nitrogen and chlorine, and we must regard these as indicating the rates of vibration, which the molecules NO_2 and ClO_2 respectively are capable of easily taking up. The absence of the absorptions due to oxygen from all compounds of oxygen seems to indicate either that chemical combination is not, as has been supposed by some chemists, a temporary relation in which the molecular groupings are continually breaking up, to be formed anew with ever-changing elementary atoms; or, that the periods of dissociation are very small compared with the periods of association. For otherwise we should expect that such compounds of oxygen as CO_2 and NO_2 must always have amongst their molecules some molecules identical with those of oxygen and capable of taking up vibrations of the same period. At least we must conclude that little, if any, of the oxygen of these and other compounds is ever out of the influence of the other components.

We have re-examined the absorption-spectrum of N_2O_4 at various temperatures, and agree to the conclusion of Bell (*Am. Chem. Journ.*, vol. vii., p. 32) that N_2O_4, whether liquid or gaseous, effects only a general absorp-

tion at either end of the spectrum, and that the selective absorptions observed with it are due to the presence of NO_2.

In order to obtain pure N_2O_4, the tube in which the liquid was sealed was placed in a freezing mixture and a large part of the liquid frozen; the remaining liquid was then drained as completely as possible into the other end of the tube, and sealed off.

It should be observed that the crystals of N_2O_4 appear colourless, and that when they are melted the liquid and superincumbent vapour are of a very pale yellow colour. As the temperature rises both liquid and vapour become, as is well known, of a deep orange, and finally of a dark reddish brown colour. We examined the spectra produced by two thicknesses of liquid and vapour—(1) by that contained in a narrow tube about 1 m.m. in diameter, and (2) by that in a tube about 1 c.m. in diameter. At 15° to 20° the vapour in the narrow as well as in the wider tube showed the well-known absorption-spectrum of fine dark lines; no absorption by the liquid in the narrow tube could be detected, and the liquid in the wide tube showed no fine lines, but several faint, very diffuse bands, unresolvable into lines with a spectroscope of three prisms. These bands had their maxima in places where the fine lines of the vapour were most intense and most closely set, so that it might be inferred that they were due to similar molecules in both cases; but that in the liquid the vibrations of these molecules were no longer sharply defined, but modified by the constraint arising from the liquid state. Some parts, however, of the spectrum of the vapour, where the lines were closely set, did not appear to be represented by any definite bands in the liquid. The liquid absorbed a good deal of blue light in a continuous manner, while the vapour only absorbed it selectively. At the red end the limit of the visible spectrum was lower for the liquid than for the gas, that is, there was more absorption of red light by the vapour than by the liquid, so much so that below a certain point the absorption by the vapour appeared continuous.

The narrow tube was next immersed in a wider tube full of glycerin, which was gradually heated. As the temperature rose, the colour of both liquid and vapour deepened, the absorptions of the vapour were stronger, and the liquid gave the same bands as had been before observed with the greater thickness. At still higher temperature the absorption of blue light, both by liquid and vapour, diminished sensibly, until at 85° the groups of lines in the blue had pretty well disappeared from the spectrum of the vapour. In fact, at 85° there was no sensible difference between the actions of liquid and vapour on blue light, it seemed only some continuous absorption. At the red end the difference between the liquid and vapour remained quite as strongly marked as at lower temperatures: if anything, more so; and the absorptions in the orange, yellow, and green were unaltered. At 90° the lines of the vapour in the green began to fade, and at 100° they were very faint; but those in the orange, as well as the corresponding diffuse bands in the liquid, were as strong as before. There was still considerably more absorption of red light by the vapour than by the liquid, as if there were a strong absorption-band in the red of the vapour which was absent in the liquid.

As the temperature rose to 110° all the lines in the vapour had become faint, and at 115° they were no longer discernible, and there was no difference between the spectra of liquid and vapour except in the red, and even here the difference was less marked than at lower temperatures. At 130° no distinction was observable between the spectra of liquid and vapour; there were no lines or bands in either, but a good deal of general absorption. Liquid and vapour were dark, and appeared much of a colour, but the meniscus at the junction was quite evident. The tube was further heated to 155°, but no further change was noticed in the spectrum. On gradually cooling the tube, at 112° the least refrangible band in the orange was seen coming in both in vapour and liquid, diffuse in both. At 100° the usual lines were well seen in the orange, yellow, and citron of the vapour, faint lines in the green, and none in the blue; and subsequently the appearances presented on heating followed in the reverse order.

A solution of N_2O_4 in carbon bisulphide gave in a thickness of 7 or 8 c.m. diffuse absorption-bands in the green and citron, ill-defined as in liquid N_2O_4 and in corresponding positions. In a thickness of 1 c.m. these bands were no longer visible.

These observations bear out the supposition that pure N_2O_4 is without selective absorption of the visible rays, and that the absorption observed is due to NO_2, both in the vapour and liquid, this absorption being modified in the liquid by the state of solution, in which the molecules have much less freedom. As the temperature rises the proportion of NO_2 increases, and at the same time the density of the vapour increases and the freedom of motion of the molecules is diminished; they are less able to assume the more rapid vibrations, and those which they do assume become less sharply defined, so that the lines fade into bands and ultimately into a general absorption.

Taking Willard Gibbs's expression ("Equilibrium of Heterogeneous Substances," *Connecticut Acad. Trans.*, vol. iii., p. 239) for the density D, in terms of the pressure in atmospheres ϕ, at temperature $t°$—

$$D = 3{\cdot}178 + \theta - \sqrt{\{\theta(3{\cdot}178 + \theta)\}}$$

where—

$$\log_{\cdot 10}\theta = 9{\cdot}47056 - \frac{3118{\cdot}6}{t+273} - \log_{\cdot 10}\phi,$$

as deduced from Deville and Troost's experiments, we find the density of NO_2 at 140° and 50 atmospheres, equal to 2, *i.e.*, equal to the density of N_2O_4 vapour at 60° and 1 atmosphere.

Dewar and Ansdell found the critical temperature for N_2O_4 to be 156°.

NOTE ON THE

THERMO-ELECTRIC POSITION OF PLATINOID.*

By J. T. BOTTOMLEY, M.A., F.R.S.,
and A. TANAKADATE, Rigakushi.

In carrying out a series of experiments on radiation of heat by solid bodies, an investigation to which one of the present writers has for some time past devoted considerable attention, it became necessary, for a purpose which need not here be detailed, to select a thermo-electric pair of metals, of which one metal is essentially platinum, as it passes through glass. Various pairs were considered, and some trials were made; and it was finally determined to make use of platinum and platinoid. The latter metal is an alloy whose electrical and mechanical properties were investigated some years ago by one of the present writers;† and since that time it has assumed considerable importance in the construction of electrical instruments and resistance coils. Partly on this account, and partly from present requirements, it became both interesting and necessary to determine the thermo-electric constant for a specimen of this alloy.

Platinoid is in composition very similar to German silver. In the manufacture of the alloy, however, tungsten is employed; and although an exceedingly minute quantity of metallic tungsten remains in the alloy, yet the properties of the substance are in many respects remarkable. The metal is capable of being polished so as to be almost as beautiful as silver in appearance, having only a slightly darker and more steel-like colour, and when it has been polished it remains absolutely un-

* A Paper read before the Royal Society, June 20, 1889.
† J. T. Bottomley, *Roy. Soc. Proc.*, 1885.

tarnished, even in the atmosphere of a large town, for years at any rate. It has very remarkable properties as to electric resistance. It possesses a higher resistance than any other known metal or alloy, while at the same time it has a very much lower temperature variation of electric resistance than any other known metal or alloy except platinum-silver alloy. It has also, as Sir William Thomson has found, very excellent elastic qualities.

Although it is not proposed to use the platinoid with any metal other than platinum in the investigation on thermal radiation above referred to, it nevertheless seemed advisable, when these experiments were being undertaken, to determine its position with respect to some other metals. It was accordingly tried as a pair with platinum, iron, aluminium, and with two specimens of copper.

A low-resistance Thomson's reflecting galvanometer was specially prepared for the purpose of the experiments. The mirror is a plane parallel mirror of very excellent quality by Steinheil of Munich. Its deflections were observed by means of a telescope with cross-wires and scale, instead of with lamp and scale. To avoid any influence of the suspending fibre (which, even though of single cocoon silk fibre, does, with short fibres, give an appreciable torsional resistance) the mirror was suspended by spider line. The suspending of a mirror, weighing with its magnet 0·2 grm., by a single spider line is a matter of some nicety and difficulty; but when it has been accomplished the result is so thoroughly satisfactory that it is easily admitted to be well worth a morning's labour.

To make the suspension, two small pieces of very thin bristle or of hard-spun silk fibre or split horsehair are attached to the ends of a suitable length of spider line recently spun by a good large* spider. By means of these attachments, which are easily seem, the spider line can be handled. It is then brought over the galvanometer mirror; and great assistance is experienced in these operations, and in operations with single silk fibres, by performing them on the top of a piece of looking-glass laid on the table. The illumination from beneath of the fibres makes it easy to do with these fine filaments that which it is otherwise scarcely possible. The fibre is attached to the galvanometer mirror with the smallest possible speck of shellac varnish, the greatest care being taken not to varnish any part of the spider line. When the varnish has dried the mirror can be lifted up by the spider line, caution being used at the moment of raising the one mirror off the surface of the other on account of the vacuum which is liable to be formed at the moment of separation. The mirror should be allowed to hang on the fibre inside a glass beaker for twenty-four hours at least, as the spider line stretches considerable for a time after the weight comes on it. A spider line which will carry a galvanometer mirror and magnet weighing 0·2 grm. may have, according to an estimate made by one of the present writers, about 1·700th of that of a single cocoon silk fibre.

For equal length and equal diameters the material of silk fibre has something like six and a half times the torsional rigidity of the material of spider line.

For the heating of the junctions a number of glass vessels were blown, resembling the flasks, with neck and condensing tube, used for fractional distillation, but with the condensing tube projecting upwards into the air, so that the steam of a liquid boiling in the flask ran back into the flask on being condensed. Into the shorter neck of the flask was introduced a cork which carried the thermo-junction and a mercurial thermometer, the thermo-junction being loosely bound to the thermometer, or, at any rate, kept in close contact with the middle part of the thermometer-bulb. The cool junction was bound to the bulb of a second thermometer, which dipped into a vessel containing water at the temperature of the laboratory. The water was kept thoroughly stirred from top to bottom by a properly arranged stirrer.

In the heating flasks the vapours of the following liquids were used:—Alcohol, water, chlorobenzol, aniline, methyl salicylate, and bromo-benzol.* The liquids were boiled vigorously, and the temperatures of the vapours were determined by means of mercurial thermometers. The mercurial thermometers were compared directly with the air thermometer.† The obtaining of a set of points of temperature by this means was very satisfactory in every case except that of the liquid of highest boiling-point, bromobenzol. In this case a curious phenomenon was observed. In spite of the fact that the vapour of the substance was rushing strongly into the condensing-tube and, indeed, out into the open air, at an elevation of 2 feet above the surface of the liquid, it was found exceedingly difficult to keep the temperature of the various parts of the boiling flask anything like uniform. The vapour formed itself into layers of different temperatures, the parts of the flask nearest the surface of the liquid being the hottest. At a height of 2½ inches above the surface of the liquid the temperature was often found to be as much as 8° or 10° C. cooler than it was just above the surface. The difficulty could, to a certain extent, be overcome by putting a cloak of fine flexible wire gauze all round the upper part of the flask; but the greatest watchfulness was needed to avoid mistakes.

In order to reduce the results obtained from the readings of the galvanometer to absolute electro-magnetic measure, a carefully prepared standard Daniell's cell was kept with its current always flowing through a known high resistance; and from time to time the galvanometer which was being used was thrown into the circuit, and the value of the galvanometer deflection determined. The electromotive force of the Daniell's cell was valued at 1·072 volts.

The results obtained are shown in curves and tables which accompany the paper.

In the curves the electromotive forces are shown as ordinates, the differences of temperature between the hot and cold junctions being indicated on the axis of abscissæ. The electromotive forces are given in C.G.S. units, and must be divided by 108 if it be desired to reduce them to volts. The differences of temperatures are given in centigrade degrees, and 0° C. is the lower limit as to temperature. The direction of the current in each of the cases represented is from platinoid to the second metal of the pair through the hot junction.

Table I. shows, in the way now well known,‡ the multiplier at any temperature centigrade which must be used as factor, with the difference of temperatures between the hot and cold junctions, in order to calculate the electromotive force in C.G.S. units. The algebraic sign corresponds with that used by Tait, and now adopted by Everett ("Units and Constants," 2nd Edition).

Table I.

Platinoid-platinum	$-925-1\cdot16\times t.$
Platinoid-aluminium	$-985-4\cdot31\times t.$
Platinoid-iron	$-2916+0\cdot86\times t.$
Platinoid-copper (A)	$-1246-5\cdot44\times t.$
Platinoid-copper (B)	$-1294-4\cdot88\times t.$

Combining the results of Table I. with those of Tait reduced by Everett, we obtain the thermo-electric distance of platinoid from lead, taken as zero, at various temperatures centigrade. If any one of the wires platinum, aluminium, iron, or copper used by us were identical with the wire of the same name used by Professor Tait, we should be able to deduce with exactness the distance of our platinoid wire from his lead wire. That, however, was not the case; and each of the secondary wires used

* The body about as large as a pea.

* Ramsay and Young, *Chem. Soc. Journ.* (*Trans.*), 1885.
† J. T. Bottomley, *Phil. Mag.*, August, 1888.
‡ Tait, *Edinburgh Roy. Soc. Trans.*, vol. xxvii., 1873, and Everett's "Units and Constants"—"Thermo-electricity."

by us gives us, as it were, a different result. Thus we have :—

Table II.

	Platinoid to lead.
From experiment with platinum	$-986-3\cdot26\times t$
,, ,, aluminium ..	$-1062-3\cdot92\times t$
,, ,, iron	$-1182-4\cdot01\times t$
,, ,, copper (A) ..	$-1110-4\cdot49\times t$
,, ,, copper (B) ..	$-1158-3\cdot93\times t$

Taking the mean of all of these, with the exception of the result for platinum, which we omit because different specimens of platinum are well known to differ thermo-electrically enormously among themselves, we obtain for the thermo-electric distance of platinoid from Professor Tait's lead wire $-1128-4\cdot1\times t$.

This result enables us to place platinoid in Tait's thermo-electric diagram. Its line is nearly parallel to those of palladium and German silver, and slightly above the latter. It is, however, to be remembered that, in all probability, different specimens of platinoid alloy would give results differing considerably from that quoted above.

Appendix. By A. Tanakadate.

The following experiment on the torsional rigidity of spider line was carried out in the Physical Laboratory of the Imperial University of Japan, 1884, and a notice of it was published in vol. ii. of *Rigaukkyokwai Tassi* ("Proceedings of the Science Society") of that year in Japanese. It has not hitherto been described in English, and the absolute determination as referred to below by Mr. T. Gray of the rigidity of silk fibre makes an estimate of the rigidity of spider line possible.

The determination of the torsional rigidity was a relative one, and the experiment essentially consisted in finding the deflection of a small magnet due to a given twist of the suspending fibre : the magnet being placed in the earth's magnetic field (0·3 C.G.S.). The deflection was observed by the usual method of the reflected image of a fine wire stretched before a lamp.

The mirror magnet was first hung by a silk fibre of 31 c.m. length, and placed in the usual way. The distance of scale from the mirror was 95 c.m. When the torsion head of the magnetometer was turned through one complete revolution (2π) in either direction from zero, the image of the reflected wire was displaced through 8 m.m. either way, or $8/2\times95=0\cdot0042$ radians, or 864".

The silk fibre was now detached from the magnet, and a spider's line (newly spun) was attached in its stead. The length was 28 c.m., the magnetometer was put into its place, and the torsion head was turned as before, but no appreciable deflection could be observed, even when the torsion head was turned through ten complete turns (20π). It was suspected then that the mirror might have been caught against sides of its case ; a close inspection, however, showed that it was quite free. The fibre was then shortened to 2·3 c.m. (about one-twelfth its previous length), and the experiment was repeated. Ten complete turns of the torsion head gave a deflection of 1·5 m.m. or $15/2\times95=0\cdot00079$ radians, 16·5".

In order to compare these deflections with each other, each deflection was reduced to that which would be given by a fibre of one c.m. in length by multiplying the deflections by the length of the fibre used. Thus, corresponding to the twist of one turn of the torsion head in a fibre of one c.m. long, we have :—

For silk fibre .. .. $864\cdot0''\times31=26800''$

For spider line .. .. $\frac{16\cdot5}{10}2\cdot3 = 38''$

From this we get the ratio of the torsional rigidity of spider line to that of silk fibre to be 1 : 710.

The diameters of the fibres were microscopically measured, and gave the following values :—

Silk fibre .. .. 0·00091 c.m.

Spider line .. .. 0·00028

If the elastic qualities of these fibres were the same, the ratio of the torsional rigidity would have come out $(28)^4 : (91)^4$, 1 : 112 ; and hence the torsional rigidity of spider line is less than one-sixth of that of silk fibre of the same thickness.

The above result gives us only a relative value of the rigidities between the two fibres. If we take the mean value of the torsional rigidity of silk fibre to be 0·0012 C.G.S., as found by Mr. T. Gray,* the torsional rigidity of the spider fibre of the above experiment will be 0·0002 C.G.S.

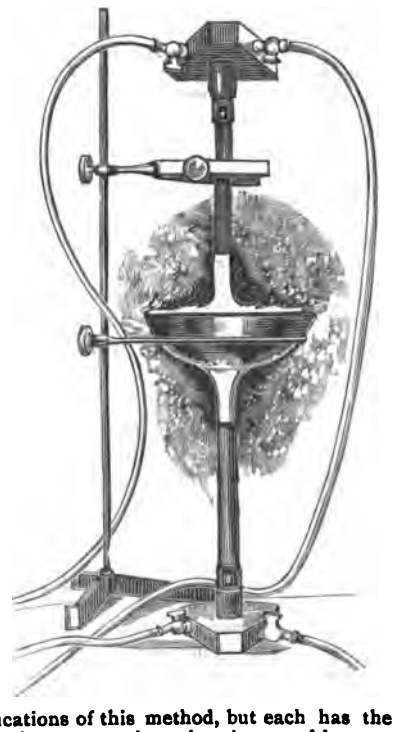
Mr. Gray's silk fibre may have had a slightly higher rigidity, as he states that it was boiled in water, while the fibre of the experiment just described was taken from those boiled in dilute potash water, as is the usual practice of preparing "mawata," which is very soft kind of silk.

SILICON IN PIG IRON.
DETERMINATION BY A METHOD OF RAPID EVAPORATION.

By Clemens Jones.

In the "direct process" of making steel, and very frequently when making foundry iron, it is necessary to determine silicon in the iron in a few minutes. To do this within the time-limit with reasonable accuracy has been found a task by no means simple.

By Ford's method, silicon can be determined in twelve minutes after taking the sample. There are several



modifications of this method, but each has the objection that during evaporation a loss is caused by spattering.

The endeavour to overcome this defect led to experiments on shortening the time by merely hastening the *modus operandi* of a standard method. Dr. Drown's admirable method was selected, and by the use of the device figured in the cut it was found that evaporation

* *Phil. Mag.*, 1887.

of 50 c.c. of nitro-sulphuric acid could be done in three minutes with complete dehydration of the silica, and very little loss, as evaporation is not carried to dryness. Moreover, the disappearance of nitric acid is marked by a strongly tinged flame reaction.

A platinum dish of 150 c.c. capacity is used. 1 grm. of borings is transferred to this, 50 c.c. nitro-sulphuric acid added, and the dish is then placed between the flames from two blast-lamps. The arrangement of the lamps calls for no description; a slight adjustment of the flames, in both distance apart and intensity, is all that is required before the right effects are secured. This being done, however, the arrangement becomes a fixture. The downward flame should be a trifle stronger than the upward one. In fact, wire gauze beneath the dish gives better results by distributing the heat evenly. A Bunsen burner may be substituted for the lower lamp. Violent ebullition is prevented by the current of heat and air upon the surface of the boiling liquid, so that by giving the dish a circular motion with a pair of tongs when nearing final expulsion of nitric acid the fumes of sulphuric acid are quickly obtained, accompanied by a sharp play of reddish yellow colour of the impinging flame. When finished, the sulphate of iron is in a thick semi-pasty state, into which hot water can be poured at once. Again placed between the flames, this is speedily dissolved and is ready for subsequent treatment.

I may add that gasolene gas was employed in the experiments.

A few comparative results are given below. The irons chosen were 1 low, 2 medium, and 1 high silicon iron. The slightly higher results by rapid evaporation are due to undissolved ferric oxide formed by the intense heat.

No. 2602. Regular method (Dr. Drown's). Silicon = 0·445 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	0·657
2.	50	4 ,,	0·639
3.	50	4 ,,	0·629
4.	25	2½ ,,	0·639

No. 3252. Regular method. Silicon, 3·858 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	3·863
2.	50	5 ,,	3·849
3.	50	3 ,,	3·765

No. 2074. Regular method.

	Per cent silicon.
1.	2·374
2.	2·384

Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	2·374
2.	50	5 ,,	2·328
3.	50	5 ,,	2·276
4.	50	4 ,,	2·320

No. 1967. Regular method. Silicon, 1·829 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	1·955
2.	50	4 ,,	2·058
3.	50	4 ,,	2·010
4.	50	5 ,,	1·810
5.	25	3 ,,	1·904
6.	50	3 ,,	1·913
7.	50	3 ,,	1·815

No. 4 of this series lost silica in igniting. No. 7 was completed in twenty minutes from the time of opening the balance case. Ten minutes was consumed in filtering, and the carbon burned off in the old way. By igniting with oxygen, and filtering more rapidly, the time for a complete determination can be undoubtedly reduced to fifteen minutes.—*Journal of Analytical Chemistry*, Vol. iii., Part 2, April, 1889.

DEPOSITS OF BARIUM SULPHATE FROM MINE-WATER.*

By FRANK CLOWES, D.Sc.,
Principal and Professor of Chemistry and Metallurgy in University College, Nottingham.

Specimens of remarkable deposits which have formed in the water-boxes of coal-mines in the neighbourhood of Newcastle-upon-Tyne have been for many years in the possession of the Museum of the Durham College of Science.

A rough analysis has been published by J. T. Dunn (*Transactions of the Newcastle Chemical Society*, vol. iii., p. 261) of an apparently similar deposit, which was formed during the autumn of 1876 in the Jane Pit at Walker. During this short period the sectional area of the box had been reduced by the deposit from seven and a half square inches to less than half a square inch, and had been in places almost completely closed. The deposit consisted of layers which were alternately white and brown, and was moderately soft. Analysis showed the percentage composition to be 90 of $BaSO_4$, 8 of $SrSO_4$, 1 of $CaSO_4$, the remainder consisting mainly of SiO_2, Al_2O_3, and Fe_2O_3. The water passing through the box at the time of the examination contained no trace of barium or of strontium.

Another similar deposit was found by Dr. Richardson (*Brit. Assoc. Report*, 1863) to contain about 90 per cent of barium sulphate and 3 of calcium sulphate, the remainder consisting of silica, alumina, ferric oxide, and moisture.

Professor Lebour states the pipes which convey water from the colliery workings of the Newcastle district are frequently entirely blocked in a short space of time with deposits, amongst which barium sulphate is seldom absent, and is often the chief constituent; and he draws attention to the fact that veins of barium sulphate are by no means uncommon in the coal measures of that district.

This deposition of barium sulphate is of interest in connection with the discovery of the sulphate as a cementing material in sandstone near Nottingham, and as no complete analysis existed of the water-box deposits in the Durham College Museum, Professors Bedson and Lebour have kindly furnished me with sections for chemical examination. The following results were yielded by the analyses:—

	Harton, box-deposit.	Jane Pit, Walker-deposit.	Newsham, box-deposit.
Loss at 100°	0·83	0·26	0·39
Loss by ignition . ..	2·15	1·51	1·95
$Fe_2O_3 + Al_2O_3$	5·44	0·12	0·37
BaO	56·72	61·30	61·09
SrO	trace	0·35	0·09
CaO	1·09	0·70	0·82
MgO	0·12	0·14	trace
SO_3	31·10	33·80	32·82
SiO_2	1·19	0·53	0·22
Alkalies, &c. (by difference)	1·36	1·29	2·25
$BaSO_4$..	86·37	93·35	93·03

The above deposits were mainly buff-coloured with thin layers of brown interposed; they were soft and loose, powder being easily detached by rubbing the surface with the finger. There was no appearance of crystallisation,

* A Paper read before the Royal Society, June 20, 1889.

but every indication of the deposit having been formed by rapid precipitation.

Professor Bedson (*Journ. Soc. Chem. Industry*, vol. vi., p. 712) and others have found barium chloride to be a common constituent of colliery waters of the district in which the above deposits have been formed. Relatively large quantities of the chloride have been found in some of these samples. The deposition may possibly arise from the admixture with such water of water containing sulphuric acid or ferrous sulphate, or both, since these substances are constantly formed by the oxidation of pyrites in the coal or in the associated shale beds. Or the barium sulphate occurring in veins in the coal measures may pass into solution under conditions yet unknown, and be deposited again as such.

Bischof mentions that hot springs may contain $BaCO_3$ and Na_2SO_4 together in solution; since at high temperatures these substances do not undergo double decomposition. Such a spring water will, however, deposit $BaSO_4$ as it cools, since at ordinary atmospheric temperatures $BaSO_4$ and Na_2CO_3 are produced by the interchange of constituents. Possibly alteration of temperature may in a similar manner give rise to the above remarkable water-box and pipe deposits.

Possibly the deposition of barium sulphate in the form of stalactite, which has occurred in some parts of Derbyshire, may be due to the same causes as these mine-water incrustations.

DETECTION AND DETERMINATION OF SODIUM HYDROCARBONATE IN MILK.

By L. PADÉ.

Sodium hydrocarbonate is the salt most commonly added to milk to prevent coagulation. In more than a hundred experiments with pure milks the author has found that a drop of decinormal sulphuric acid was always sufficient to render the ash of 10 c.c. of milk acid. It might seem, therefore, that by determining the alkalinity of the soluble ash of a milk we might determine the hydrocarbonate added. The author has, however, never reached this result, and according to his experiments in pure milk, mixed with 1 grm. per litre of sodium hydrocarbonate, we never find more than 0·34 to 0·40 grm. of alkalinity calculated as sodium hydrocarbonate. This process, therefore, though sufficient for detecting the presence of the salt, has no value for its determination. When seeking the causes of the disappearance of the greater portion of the alkalinity of the soluble ash of a milk containing sodium hydrocarbonate, the author has found an exact process for the determination of the salt. During the ignition about two-thirds of the sodium carbonate are transformed into sodium phosphate and calcium carbonate by reacting upon the calcium phosphate of the milk. Hence the ash of a milk to which sodium hydrocarbonate has been added contains sodium phosphate. But as the soluble ash of a pure milk is very slightly alkaline, and contains only traces of phosphoric acid, it is sufficient, in order to find exactly the quantity of sodium hydrocarbonate which has been added, to take the alkalinity of the ash and determine the phosphoric acid which they contain.

To effect these two determinations the author has arrived at the following method:—

He incinerates 25 c.c. of the milk and determines the alkalinity with decinormal sulphuric acid; the volume obtained in c.c., multiplied by 0·0084 grm., gives the quantity of hydrocarbonate not transformed into sodium phosphate contained in 25 c.c. of milk, and on afterwards multiplying by 0·0336 we obtain the percentage. In this neutral solution, mixed with 2 c.c. of a slightly acetic solution of sodium acetate at 10 per cent, the phosphoric acid is determined by means of standard uranium acetate.

The uranium solution is standardised so that 1 c.c. corresponds to 0·01 grm. of sodium hydrocarbonate in 100 c.c. of milk when the determination is effected in 25 c.c.

The standard of the liquid is derived from the transformation of sodium hydrocarbonate into phosphate according to the following formula—

$$4(CO_3NaH)+(PO_4)_2Ca_3= =2PO_4Na_2H+3CO_3Ca+CO_2+H_2O,$$

according to which 336 grms. sodium hydrocarbonate yield 284 grms. sodium phosphate, or for 1 grm. of hydrocarbonate, 0·84523 sodium phosphate containing 0·4226 grm. phosphoric acid (P_2O_5).

The uranium liquid is standardised, volume for volume, with a solution containing, per litre, 3·11 grms. sodium-ammonium phosphate. This weight of sodium phosphate is equivalent to 2·5 grms. sodium hydrocarbonate. Then, if we make the determination upon 25 c.c. of milk, 1 c.c. of the standard solution of uranium or of sodium phosphate answers to 0·01 grm. hydrocarbonate in 100 c.c. of milk.

The determination is made in the ordinary manner, either by spotting with ferrocyanide or by means of tincture of cochineal. The latter process is the more sensitive, on account of the dilution of the uranium liquid.

On adding to the weight per cent of alkalinity as found that given directly by the determination of the phosphoric acid, we obtain the total percentage weight of the sodium hydrocarbonate added to the milk. The greatest irregularity the author has ever observed in using this process has been an excess of 0·008 grm. of hydrocarbonate per cent.—*Comptes Rendus*, cix., p. 154.

ON THE AMMONIO-COBALTIC TUNGSTATES AND VANADATES.

By ADOLPHE CARNOT.

A solution of ammonium tungstate, poured into a dilute solution of a purpureo-cobaltic salt acidified with acetic acid, produces at once an abundant rose-coloured precipitate analogous to that produced by the molybdate. When the reagent has been employed in sufficient quantity the liquid gradually becomes clear and colourless; it no longer contains nickel and gives no black deposit with ammonium hydrosulphate. The rose-coloured precipitate, if dried at 100°, turns lilac; if heated progressively to redness it loses water, ammonia, and oxygen, and passing through dark blue and blackish green tints, it finally becomes light greenish yellow. It remains infusible and undecomposable at a bright red heat. When cold, the ignited matter is of a greyish blue. It answers to the formula $CoO,5WO_3$. The analysis of the precipitate when merely dried gave $Co_2O_3,5NH_3,10WO_3+9HO$.

The salts of cobaltous and nickelous oxides are not precipitated under the same circumstances by the tungstate. This reaction might therefore serve for the separation of the purpureo-cobaltic compound, as it has been already indicated for the molybdate. But it is more difficult to obtain a product of unvarying composition. On the one hand, ammonium tungstate being sparingly soluble in water at the common temperature (1 part in 32), and much more soluble at 100°, we are in danger of producing a deposit of this tungstate, and consequently an excess of the ignited product if we employ a solution recently prepared. If, on the other hand, the solution is not sufficiently acid, there may be produced a crystalline deposit of cobaltous or nickelous tungstate, both causes of error, of which there is less risk in using the molybdate.

In ammoniacal liquors the reactions of the cobalt and

nickel salts are quite different with the tungstate than with the molybdate. A purpureo-cobaltic salt gives an insoluble rose precipitate in presence of a slight excess of ammonia as well as in an acetic liquid. A cobaltous salt gives a crystalline precipitate of a yellowish grey, which alters on exposure to the air and becomes rose on drying. This is a double ammonium-cobalt tungstate—

$$15WO_3.2CoO.8NH_4O+3HO.$$

A nickel salt gives a crystalline precipitate of a slightly bluish tint, which is formed slowly. Along with it ammonium tungstate is often deposited in white needles.

Vanadates.

Ammonium vanadate produces with ammonio-cobaltic salts in a slightly acetic solution an orange-yellow precipitate which answers to the formula—

$$Co_2O_3.5NH_3.5VaO_5+9HO.$$

This compound, if carefully heated to dull redness, becomes agglomerated and swells up much. It takes at the same time a blackish grey tint, which in a short time passes to a rose-brown. If heated above dull redness the product melts completely and becomes blackish. After and before fusion its composition is $2CoO.5VaO_5$.

The cobaltous and nickelous salts form slowly a crystalline deposit in an acetic liquid, but they are at once precipitated on saturating the liquid with ammonia.

Cobalt yields under the same conditions a green precipitate of cobaltous vanadate, which is readily peroxidised by the air and becomes yellow. If dried to 100° it takes a reddish brown tint, and yields, on fusion, a black compound, CoO_2VO_5.

Nickel gives an orange-yellow precipitate which turns brown when dried at 100° and black on fusion—$NiO,2VO_5$.

This nickel divanadate is very easily obtained on saturating with a slight excess of ammonia a solution which was originally acetic, and, in consequence, of a brown colour. A monovanadate, NiO,VO_5, may be obtained less easily on using a larger quantity of ammonia. No precipitate appears if we use a colourless vanadate, neutral or slightly ammoniacal, pouring it into a solution of nickel, likewise ammoniacal.

There appears to be formed by the action of free acetic acid a deeply coloured ammonium divanadate, which, in presence of a salt of nickel, yields, on saturation with ammonia, a precipitate of nickel divanadate.—*Comptes Rendus*, cix., p. 147.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ

(Continued from p. 71).

Foreign Sources.

In this, the fifth of the annual reports on precious stones in the United States, which have done much toward awakening a wide-spread interest in American gems, it was thought well to give a brief sketch of some of the most important changes which are taking place in precious stones at the principal sources, which are usually foreign.

Diamonds.—The author of the "Arabian Nights" undoubtedly thought that he was imagining the wildest and most improbable things when he described the collection of such treasures in the Valley of Diamonds by "Sinbad the Sailor." Yet when compared with the African mines this profusion of wealth has paled into utter insignificance. A glimpse at these new valleys of diamonds will be interesting. The primitive method of washing was carried on for centuries by thousands of slaves, who, like those who built the pyramids, were driven by a master mercilessly goading them on, whip in hand. To-day we have the most ingenious and powerful machinery, which allows fewer diamonds to escape than would the keenest and most disciplined army of washers.

At the Kimberley diamond mines in South Africa wonderful progress has been made in the last decade. About 1877 the work of consolidating the different companies began. Originally the mines were worked as 3238 separate claims, each 31 feet square, with a 7½ foot roadway between every two claims; now these are all united in about forty companies. A mine in the early days was a bewildering sight. Miles of wire cables running from individual claims were stretched across it in all directions; to these were attached the buckets for carrying the earth, reef, or wall rock of the mines, and at times water. Some of the claims were almost level with the surface, while others next to them might be cut down 200 feet, and others only 100 feet, yet all being worked independently. At the sides were endless belts with pockets for carrying the earth. One of the results of this independent system of working was that rock was dropped so recklessly that it is said to have been as dangerous as the battlefield to stand around the edges of the claims. Not only was the loss of life great from this source, but also from the falling of immense masses of reef, loosened by the blasting, which sometimes buried a score of men at once. But improved methods were gradually introduced. Steam railroads were run into the mine, and parts of it were levelled down. Millions of tons of reef required removing, and the only way to accomplish this was to assess every company in the mine proportionately. At first many mistakes were made, if mistakes they can be called when the problems offered for solution were entirely new and untried. The yellow or surface soil which overlaid the blue stuff pulverised so readily that it could be taken to the washing machine direct; but as the claims were extended down into the blue rock this proved harder, and dynamite became necessary. Immense quantities of it are now used for blasting. Through careless storing, 30 tons of dynamite, 10 tons of blasting-powder, and gelatin, in all worth 80,000 dollars, exploded on January 10, 1884, with terrific effect; the smoke column, 1000 feet high, was visible at the River diggings, 35 miles distant.

After the earth is raised it is put on the sorting ground, where it is partially disintegrated by water and the action of the atmosphere. It is then further broken up by hand and taken to the "compound" or diamond-sorting machine. After being more finely broken up it is passed down into large vats containing immense centrifugal wheels, by which, as they rapidly revolve, the rock is finely divided. The lighter minerals, such as quartz, mud, and mica, are then floated out, while the diamonds, garnets (some of which are exceedingly rich in colour, and of large size, and are sold under the name of cape rubies), and other heavy minerals, are concentrated in the lower part of the "compound." So thoroughly does this pulverise the rock and earth that all the diamonds, even those of the size of a pinhead, are saved.

A prize of £5000 was offered for the best tunnel or shaft system for use at the Kinberley mines, and the prize was awarded to the Jones system, which is sunk on the coffer-dam principle. At present there are seven shafts and inclined planes in the Kimberley mine alone, all sunk at some point in the reef outside of the mine. From 11,000,000 to 13,000,000 gallons of water are annually hoisted from the Kimberley mine at a cost of sixpence per load of 100 gallons.

In addition to many miles of aërial tramways, there are over 170 miles of tramway around the four Kimberley mines, 2500 horses, mules, and oxen, and 350 steam-engines, representing 4000 horse-power, are employed in the works. For labour, £1,000,000 are annually expended, and over £1,000,000 for fuel and other supplies. The gross capital of the companies is nearly £10,000,000. Over 10,000 natives, each receiving £1 per week, and

* Abstract from "Mineral Resources of the United States."

1200 European overseers at an average wage of £5, are employed. It is now proposed to consolidate all the companies into an enormous diamond trust, with a capital of £10,000,000, but at the present quotations of the shares of the company they are valued at over £14,000,000. The supposition long held that this unification would ultimately be accomplished is partly confirmed by the report, this spring, that the house of the Rothschilds, of London, is about to put in operation a project for the consolidation of the diamond mines into one gigantic trust for the regulation of prices and production.

The South African mines yielded during the last ten years 27,878,587 carats, valued at £31,717,341. The yield for 1887 was 3,646,899 carats, worth £4,033,582 at a valuation of £1 2s. 1¼d. a carat. In December, 1887, a single sale of rough diamonds was recorded of £150,000, and in February, 1888, of £250,000, or 750,000 dollars and 1,250,000 dollars, respectively. The average value of a carat of diamonds for some years from the respective mines has been as follows:—

Average Value of a Carat of South African Diamonds.

	s.	d.
Kimberley mine	17	6½
De Beers mine	17	8
Bultfontein..	18	2½
Dutoits Pan	24	7½
River digging	47	6

The product of the latter mine, while only $\frac{1}{100}$ of the weight in carats, was worth $\frac{1}{8}$ of the entire product, the stones averaging much finer quality.

The approximate annual yields for the last ten years have been as follows:—

Years.	Carats.	Value.
1878	2,540,000	£2,672,734
1879	2,610,000	2,864,631
1880	3,030,000	3,168,000
1881	3,315,000	4,200,000
1882	2,385,000	3,500,000
1883	2,312,000	2,359,466
1884	2,204,786	2,228,678
1885	2,287,263	2,228,680
1886	3,047,639	3,261,570
1887	3,646,899	4,033,582
River digging	500,000	1,200,000
Total	27,878,587	31,717,341

Not only has the yield of the African mines been great, but the diamonds have been of much larger average size than those from any of the old mines. The finding of a 17-carat stone in the Brazilian diggings was sufficient to secure the freedom of the fortunate slave who found it; but stones of this size are found by the hundred here. A 100-carat stone scarcely creates as much excitement as a stone of one-fifth the size did in Brazil.

It is estimated that from one-fifth to one-quarter of all the yield never reached the proper owners, as the native diggers swallow and conceal the diamonds in every possible manner. Hence it became necessary for the companies, in self-defence, to take extraordinary precautions against this great loss, and overseers or special searchers were appointed, who made the most thorough examination of all who left the mines. The natives use most ingenious methods for the concealment of the gems. On one occasion some officers, suspecting that a Kaffir had stolen diamonds, gave chase and caught up with him just after he had shot one of his oxen. No diamonds were found upon the Kaffir, it is needless to say, for he had charged his gun with them, and after the disappearance of the officers he dug them out of his dead ox. Diamonds have been fed to chickens, and a post-mortem recently held over the body of a Kaffir revealed the fact that death had been caused by a 60-carat diamond which he had swallowed. Early in the history of the mines a detective force, consisting of men, women, and children, was formed, and the severest punishment is still inflicted on transgressors of the Diamond Act. None but those authorised by law, termed patented agents, less than fifty in number, are allowed to purchase, or even to possess, rough diamonds at Kimberley.

The actual loss of diamonds would not have been so great but for the irregular diamond buyers, or "I.D.B's.," as the "fences" are called, who sent the stones to England and undersold the company in the London market. It was a question at one time whether the mines could be profitably worked under such disadvantages. Within the last two years, however, this pilfering has been in great measure checked by the adoption of what is known as the compound system, by which the "boys" are housed and fed under contract for a certain term, provided with amusements and liquor, and thus kept apart from the influences of the vicious whites. Now the visitors who buy from natives diggers what they suppose to be valuable diamonds and secrete them until they have passed beyond the reach of the officials, find to their disgust that they have purchased fac-similes in glass, perfect even to the characteristic yellow tint peculiar to many diamonds from this locality.

Diamonds weighing 38,000,000 carats, or over 7½ tons, have been found here. In the rough their aggregate value is £50,000,000, and after cutting £100,000,000, or nearly 500,000,000 dollars more than the world's yield during the two preceding centuries. Of the whole yield not more than 8 per cent can be said to be of the first water, 12 per cent of the second water, 25 per cent of the third, while the remaining 65 per cent is called bort, a substance which, when crushed to powder, is of use in the arts for cutting hard substances and engraving. This must not be confounded with the carbon (carbonado) found in Brazil, an uncrystallised form of the diamond, which, from its structure, is adapted for use in drills for boring and tunnelling rocks, &c., and has never yet been found in South Africa. It is worth from six to ten times as much as bort.

More diamonds weighing over 75 carats after cutting have been found since the African mines were opened than were known before. The Victoria, the Great White, or the Imperial Diamond, is supposed to be from South Africa. Concerning its early history very little is known; in fact, where the stone was found is only a matter of conjecture—a remarkable circumstance when we consider that it is the largest brilliant in the world. The original weight of the stone was 457½ carats, or $3\frac{1}{10}$ troy ounces; after cutting, 180 carats, valued at £100,000.

On March 28, 1888, there was found in the De Beers mine an octahedral crystal of diamond weighing 428½ carats; it is not entirely white, having a slight yellow tinge. It was valued at £3000. From its form it is believed that it will cut into a brilliant of 200 carats, hence it will be the largest known.

Production of Diamonds at the Griqualand West Mines, Kimberley, De Beer's, Dutoits Pan, Bultfontein, and St. Augustine, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value.	Average per carat.	
		£	s.	d.
1882, four months..	856,353⅜	1,119,210	26	1½
1883	2,312,234½	2,359,466	20	4⅜
1884	2,204,786½	2,562,623	23	2⅜
1885	2,287,261	2,228,678	19	5⅜
1886	3,047,639⅜	3,261,574	21	5
1887	3,646,899⅜	4,033,582	22	1½
Total	14,355,174½	15,565,133	21	8½

Comparative Yearly Exports of Diamonds from January 1, 1883, to December 31, 1887.

Years.	Carats.	Declared value. £	s.	d.	Average per carat. s.	d.
1883	2,413,953⅜	2,742,521	1	0	22	8⅝
1884	2,263,086⅝	2,807,288	3	4	24	9½
1885	2,440,788⅛	2,492,755	13	2	20	5
1886	3,135,432¾	3,507,210	14	0	22	4
1887	3,599,036¼	4,251,837	14	6	23	7¼
Total ..	13,852,897⅛	15,801,613	6	0	22	9⅜

Imports of Diamonds into Kimberley from the River Diggings, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value. £	Average per carat. s.	d.
1882, four months ..	5,742⅜	6,010	20	11⅛
1883	14,800⅜	37,112	50	1⅜
1884	19,710⅜	57,639	58	5⅜
1885	27,992	56,123	40	1⅛
1886	38,673⅛	84,829	43	10¼
1887	46,171½	95,433	41	4⅛
Total	153,090½	337,146	44	0½

Summary of Imports of Diamonds into Kimberley from September 1, 1882, to December 31, 1887.

Whence imported.	Carats.	Value. £	Average per carat. s.	d.
Colony, England, &c. ..	130,133⅜	127,831	19	7⅜
Orange Free State ..	306,660⅜	505,428	32	11½
River diggings (Barkly West)..	153,090½	337,146	44	0½
Total	589,884⅜	970,405	32	10⅜

Summary of Production of Diamonds at the Griqualand West Mines for the Year 1887.

Mines.	Carats.	Value. £	s.	d.	Averege per carat. s.	d.
Kimberley ..	1,333,832½	1,410,207	12	1	21	1⅜
De Beer's ..	1,014,048	1,022,878	6	5	20	2
Dutoits Pan ..	696,576½	987,283	17	8	28	4⅛
Bultfontein ..	602,246	612,962	18	6	20	4¼
St. Augustine.	197	250	0	0	25	4¼
Total ..	3,646,899⅜	4,033,582	14	8	22	1¼

Production of Diamonds, Kimberley Mine, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value. £	Average per carat. s.	d.
1882, four months..	380,955¼	456,420	23	11½
1883	947,817⅜	846,705	17	10¼
1884	642,438	634,332	19	9
1885	523,774¼	458,858	17	6¼
1886	889,864	883,503	19	10¼
1887	1,333,832½	1,410,207	21	1⅜
Total	4,718,681⅛	4,690,025	19	10¼

The diamond mines at Salabro, Brazil, known as the Canavieiras, were discovered in 1882 by a poor miner who had worked in the earlier mines, now nearly exhausted. They are situated at a distance of two days' journey from Canavieiras, near the river Pardo, and the gems are found at a depth of about 2 feet in a red gravel. They are very fine in quality, and are remarkable for their purity and whiteness, the crystals being of such a form that scarcely any cleaving is necessary.

History repeats itself, and as, when the Brazilian mines were first discovered, they sent the stones to India to enter the European markets in European wrappers, so Bultfontein diamonds were sent to Canavieiras to be shipped to Europe as the product of that mine.

So great was the rush for these mines at first that, notwithstanding the rumours of a malarial climate and epidemic diseases, by the end of the first year 3000 miners were at work where shortly before was a virgin forest. For a time even this number was exceeded. The other Brazilian mines have been only slightly worked of late years.

The recent concentration of some of the diamond mining companies in South Africa in their efforts to regulate the production and price has led to an increased interest in mines located in Brazil and India. During the past year the Madras Presidency Diamond Fields Company (Limited) has been organised with a capital stock of £190,000. To prove that the Indian mines are not yet exhausted, operations will be commenced at the Wadjra Karur field in the Madras presidency. On this field of 554 acres was found a very fine 67¼ diamond crystal which furnished a 25-carat stone, called the Gow-do-Nor, valued by the company at £15,000. An English company has recently been formed, under the name of the "Hyderabad Deccan Mining Company," to work the mines in Krishna Valley, India, where it is thought the famous Koh-i-noor was found.

Diamonds have been found in the Tertiary gravels and recent drift near Bingera, in Inverell, Australia; also along the Cudgeon river, 160 miles north-west of Sydney, and in other districts. The colours are white, straw, yellow, light brown, pale green, and black. The largest stones yet found were cut into gems weighing 3¼ and 3 carats, respectively. A trial made by the Australian Diamond Mining Company produced 190 diamonds, weighing 197⅜ carats, from the washing of 279 loads of earth. These Australian fields can scarcely be called productive as yet, nor from present appearances do they seem likely to become formidable competitors of the South African fields.

India, Borneo, and Australia are now yielding very few diamonds, probably not more than 1 per cent of the entire product. These three countries, together with Brazil, yield probably less than 10 per cent of the total output.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 5, July 29, 1889.

A New Process for the Volumetric Determination of Silver, Mercury, and Thallium by Means of Potassium Iodide.—Adolphe Carnot.—This paper will be inserted in full.

Researches on the Sulphites.—P. J. Hartog.—The author has formed the potassium-, the sodium-, and the normal double potassium-sodium salts, and studied them chiefly from a thermo-chemical point of view.

Synthesis of Some Selenium Compounds of the Aromatic Series.—C. Chabrié.—The author has undertaken the synthesis of compounds in which the selenium is directly combined with the carbon of the cyclic nucleus. The chloride, $SeCl_4$, reacts upon benzene, yielding the subchloride and the mono-, bi-, and trichlorobenzenes, which are separated by water from the subchloride. The chloride, which chlorinises benzene and toluene, acts in a similar manner upon the fatty carbides. In presence of aluminium chloride $SeCl_4$ yields with benzene selenophenol, phenyl-selenide, and a red oil which distils at 245° to 250°, and has the composition $Se_2(C_6H_5)_3C_6H_4Cl$.

Selenium does not react upon benzene in presence of aluminium chloride, as do oxygen and sulphur.

The Oxidising Action of Nitrosocamphor under the Influence of Light.—P. Cazeneuve.—Nitrosocamphor is decomposed under the influence of light. If dry it yields nitrous gas. If mixed with water it gives off pure nitrogen, and oxidises, at the same time, bodies with which it comes in contact. The author has studied this phenomenon in the cases of alcohol, mannite, glycerin, and the oxalic and formic acids. The facts observed may be compared with certain chemical actions in plants. The formation of chlorophyll and of the colouring-matters of flowers which appears connected with the intervention of light, may be the result of oxidising actions effected by the intervention of oxygen compounds decomposable by light.

On the Isocamphols. Influence of Solvents upon their Rotatory Power.—A. Haller.—The modifying power of solvents, if null in case of any given body, may be exerted upon one or several of its isomers. In the case of certain racemic compounds it may throw a light upon the nature of the compounds which concur in the formation of these optically inactive bodies.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

Contributions to Technical Gas-Analysis.—Clemens Winkler.—This memoir will be reproduced at length as early as possible.

The Density-numbers Discovered by J. A. Groshans.—Dr. G. Th. Gerlach.—Concerning this important paper we can at present merely say that the term density-number does not mean the same as density or specific gravity. The author has expressed the view that with the exception of H, C, and O probably every element consists of several micro-particles, and that of such chlorine has 4, bromine 9, and iodine 15.

Convenient Preparation of Chromium Chloride.—A. Vosmaer.—The author obtains Cr_2Cl_6 in any desired quantity by passing chlorine gas over heated chrome iron. In a combustion-tube the product can easily be obtained pure, as the ferric chloride is much more volatile and the manganous chloride much less volatile. The author uses a chrome iron containing about 21 per cent of chromium. Care must be taken that the tube does not become blocked up. The product obtained was quite insoluble in water, and consisted of long beautiful violet needles of a velvet-like lustre. The author attempted to obtain tungsten hexachloride in a similar manner from tungsten-iron. The result was a mixture of scarlet needles of $WOCl_4$ and of yellow WO_2Cl_2. The former compound passes quickly into the latter.

Determination of Silicon and Iron in Cryolite.—R. Fresenius and E. Hintz.—The authors attempted the solution of this question by decomposing the samples with sulphuric acid in a suitable apparatus and conducting the volatile products, hydrogen fluoride and silicon fluoride, into ammonia. The bulk of the silicon, however, remained in the residue in the form of fine sand, and only relatively small quantities were volatilised. The following method was used with success. The apparatus employed was a stout lead tube,, of 2·6 c.m. internal diameter, bent U-shape, and with its lower curved part completely bedded in a sand-bath. The two limbs of the tube were closed with perforated caoutchouc stoppers, in each of which a smaller lead tube was fixed air-tight. One limb was thus connected with a sulphuric acid washing-bottle, whilst to the other were joined two other lead tubes similar to the decomposition-tube, but having only an internal diameter of 2 c.m. The furthest of these tubes was again connected with a glass U-tube containing water and with an aspirator, so that a slow current of air can be drawn though the apparatus. Before using, the decomposition-tube may be charged with water and heated to 200° C., so that its inner surface may become covered with lead sulphate. After this it may be washed with water and is ready for use. The two narrower leaden tubes of the apparatus are then charged with ammonia; a weighed quantity of the cryolite—say 5 grms.—is introduced into the decomposition-tube, covered with 15 c.c. of undiluted sulphuric acid, and the apparatus is closed air-tight. The aspirator is set in action so that a slow current of air passes through the apparatus; the sand-bath is heated to 200°, the temperature being indicated by a thermometer plunged into the sand-bath. After heating for two hours and keeping up the current of air the apparatus is let cool, the contents of the decomposition-tube are rinsed out into a platinum vessel, and compounds of alumina, &c., are dissolved by the application of heat, and, if needful, by the addition of a few drops of hydrochloric acid. The residue, containing the bulk of the silica, is filtered off, washed, and melted with sodium carbonate. As the residue possibly may not be quite free from fluorides, the alkaline reaction of the watery solution of the melt is almost entirely but not quite neutralised at a boiling heat with hydrochloric acid, and the silica is chiefly separated out by evaporation. To the filtrate there is now added a solution of zinc carbonate in ammonia, and the liquid is concentrated until all ammonia is expelled. The separation of silica from the last precipitate is effected in the known manner by solution in nitric acid, evaporation, re-solution in nitric acid, and filtering off the residual silica. The part of the melt which is insoluble in water is dissolved in silica, and here also the silica is determined in the usual manner. The portions of silicon have still to be determined which were volatilised as silicon fluoride, and retained in the lead tubes charged with ammonia. On emptying the tubes the ammoniacal liquid was found turbid from the presence of lead sulphide and sulphate, both arising from the previous treatment of the tube with sulphuric acid. Lest small quantities of silica should escape determination this precipitate is filtered off, ignited along with the filter, the ash evaporated down with a few drops of nitric and sulphuric acids, and the lead sulphate thus formed is extracted with ammonium acetate. Any residue is added to the silica to be weighed. The ammoniacal solution is mixed with so much sodium carbonate that, after the expulsion of the ammonia, the reaction may still be distinctly alkaline, and here, as above, the silica is separated by means of an ammoniacal solution of zinc. The four or five portions of silica are weighed together and tested as to their purity by volatilisation with sulphuric and hydrofluoric acid. Iron in cryolite is determined by dissolving in sulphuric acid and filtering off the insoluble residue. This residue is fluxed with sodium carbonate, the melt is softened with water, the silica is separated with hydrochloric acid, the hydrochloric and sulphuric are mixed together, and the iron present in solution is per-oxidised, if needful, with chlorine-water. On pouring this liquid into strong hot potassa-lye there is obtained a small precipitate, which is washed and dissolved in hydrochloric acid. After the addition of tartaric acid pure iron sulphide may be precipitated by means of ammonia and ammonium sulphide, converted into ferric oxide in the ordinary manner, and weighed.

Examination of Vermicelli for Foreign Colours.—L. Cavedoni (*L'Orosi*).—100 grms. of the sample are dried, powdered, treated with 200 grms. alcohol for twenty-four to thirty-six hours, and the filtrate is concentrated to 10 c.c. If saffron is present the extract is yellow and has an odour of saffron. The yellow colouring-matter of safflower does not dissolve in alcohol. The yeliow of turmeric is taken up by alcohol, and the extract smells of turmeric. Coal-tar colours dissolve in alcohol, and can be extracted from the concentrated aqueous residue by amylic alcohol. If Martius yellow is present the aqueous extract is decolourised by hydrochloric acid and the yellow colour is restered on neutralising with ammonia.

A Substitute for the Calcium Chloride Tube in Organic Analysis.—Jos. Preusser.—The apparatus cannot be intelligibly described without the accompanying figure.

The Determination of Thallium and Mercury.—Dr. W. Feit.—Thallium is generally determined by precipitation as thallous iodide, which is then dried at 110° to 120° on a weighed filter and weighed. The results agree well together, but they are rather too low, as the iodide is not absolutely insoluble, even in acetic or ammoniacal water. The author proposes a method founded on the reaction of the salts of thallium oxide with potassium iodide. If the solution of a thallic salt is mixed with potassium iodide there is a greenish black precipitate consisting of a mixture of thallous iodide and free iodine. The liberated iodine is converted into hydrogen iodide by an excess of arsenious acid and the excess is titrated back with iodine solution. For the execution of the analysis the author uses a solution of arsenious acid approximately decinormal and an approximately 1-50th normal solution of iodine accurately standardised with this solution. To prepare the arsenious solution 4·942 grms. of arsenious acid are dissolved in an excess of alkali in a litre flask, neutralised with hydrochloric acid, and filled up to the mark with sodium hydrocarbonate. The standardising is effected with absolutely pure bromine, which is weighed for this purpose in a small glass globe closed before the blowpipe after filling. The mean of several determinations showed that 1 c.c. of the solution contains 0·004884 grm. arsenious acid, a quantity corresponding 0·0125055 iodine. Four atoms of iodine correspond to two atoms of thallium, *i.e.*, 506·16 grms. iodine=407·2 grms. thallium. Hence 1 c.c. of arsenious acid=0·0100605 grm. thallium. The solution of iodine was obtained by diluting an approximately decinormal solution of iodine, carefully standardised with arsenious acid, so that 5 c.c. of the iodine solution exactly correspond to 1 c.c. of the arsenious acid. In order to carry out the method it is preferable to dissolve the substance as thallic sulphate. In case of any other thallic salt at least so much sulphuric acid must be added as would be required for the formation of thallic sulphate. This is absolutely necessary in case of thallic chloride, bromide, or iodide. If the corresponding thallous compounds are present after introducing the sulphuric acid bromine-water is added until the liquid has a distinct yellow colour, and it is then boiled until all free bromine is expelled and the liquid is colourless. If the compound is insoluble in water the insoluble thallous salts can be readily converted by bromine into soluble thallic salts. If, after the expulsion of the bromine, there appears a turbidity from the separation of thallium hydroxide a few drops of sulphuric acid are added. An excess of potassium iodide is added in the cold, the free acid is neutralised with sodium hydrocarbonate, an excess of which is added, and so much of the arsenical solution is dropped in with the burette as corresponds to the highest proportion of thallium in the substance. At first there is no change of colour, but in a short time the liquid begins to turn to a lighter colour. The decomposition is hastened by frequent agitation. If a few c.c. of arsenious acid have been added in excess the transformation is more rapid. In a quarter of an hour at furthest the precipitate is a pure yellow. As in titrating back this precipitate hinders the exact detection of the final reaction, it is best to conduct the operation in a measuring-flask, filling up to the mark as soon as the precipitate has assumed a pure yellow colour, mixing the liquid and filtering through a folded filter into a dry beaker. An aliquot portion is then titrated back with solution of iodine and starch. The liquid must on no account be filtered off until the precipitate is of a pure yellow colour. The method is, of course, not applicable if metals are present which react with arsenious acid, either becoming reduced or forming insoluble arsenites. Such metals may be previously removed by means of sodium hydrocarbonate. The author has applied the same method to the analysis of mercurial compounds, but the results obtained did not agree very closely.

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THE CHEMICAL NEWS.

VOL. LX. No. 1552.

ON THE NATURE OF THE REACTION BETWEEN SOLUTIONS OF FERRIC CHLORIDE AND POTASSIUM IODIDE, AND THE VOLUMETRIC TITRATION OF IRON IN THE FERRIC STATE.

By D. J. CARNEGIE, M.A.

IN standard text-books* the reaction between solutions of ferric chloride and potassium iodide is formulated as follows:—

$$FeCl_3+KI=FeCl_2+KCl+I \quad . \quad . \quad . \quad (I.)$$

In many of the original papers on this reaction the same idea as to its mechanism prevails; witness, for example, the following sentence from a paper by Braun:—"und die Eigenschaft des Eisenchlorids durch Kalium Iodid in Eisenchlorür reducirt zu werden."

Duflos was the first to point out the applicability of the action between KI and $FeCl_3$ to the ready determination of iron in the ferric condition; translated into modern notation his original representation of the reaction appears as—

$$FeCl_3+3KI=FeI_2+I+3KCl \quad . \quad . \quad . \quad (II.)$$

In both these equations the ratio Fe : I is the same, but in the former the iron after the reaction exists as ferrous chloride, whereas the latter represents the residual iron as existing in the form of ferrous iodide. In short, in equation I., KI figures as a *direct reducing agent*—a *rôle* with which this substance is not generally credited.

Now it seems to me that the second equation is the more probable; it may conveniently be split up into two stages, one stage representing a double decomposition, the other a dissociation—

$$FeCl_3+3KI=FeI_3\dagger+3KCl.$$
$$FeI_3=FeI_2+I.$$

Duflos's method, modified in several of its details by Mohr, Braun, Spreng, and others, exists to-day as one of the standard methods for the estimation of iron, and the *modus* is described in all text-books, the representation of the fundamental action given being equation I. and not equation II. On several occasions I myself, and others working with me, have employed the method as described with very indifferent results. Reference to the original papers on the subject showed them to be vague and conflicting with respect to the best amount of KI to use, the necessity of nearly neutralising the iron solution, &c. These facts, coupled with the *à priori* improbability of KI acting as a direct reducing agent, induced me to re-investigate the action with a view to determining the conditions of its applicability as a volumetric method, and its true, as distinguished from its merely empirical, nature.

It is a well-known fact that when acidified solutions of KI are allowed to stand in contact with the air free iodine soon makes its appearance. This decompositon, *cæteris paribus*, takes place more readily the higher the temperature. So far as I know, this reaction has not been studied with respect to its bearing on iodometric processes. Some preliminary experiments on this point seemed therefore advisable. The accompanying table, which is sufficiently self-explicit, exhibits the results of these experiments. I do not claim absolute, but merely relative, accuracy for the results.

<1 signifies that one drop of the thiosulphate solution used (12 grms. per litre) was more than sufficient to react with the free iodine.

The KI used was free from iodate, and the solution contained 60 grms. per litre.

The dilute HClAq contained 0·1339 grms. HCl per c.c.

The ferrous iodide solution was made by allowing 2·27 grms. iodine to react with excess of *ferrum redactum* in 50 c.c. water. Thus 10 c.c. of the resulting solution contained 0·1 grm. Fe. The solution was allowed to stand in contact with the iron, and was drawn off as required by a "reverse filter."

It appears, therefore, that digestions involving acidified solutions of KI should always be carried out in an inert atmosphere of CO_2. This is an important point, which, I think, is not mentioned in English handbooks. The presence of this inert atmosphere is not of so much importance when distillation is used instead of digestion, provided that in the distillation the heating be rapid and the boiling-point soon reached. The form of distilling apparatus used will be mentioned later on. A somewhat curious fact in this connection is that acids will liberate iodine from fairly strong and hot solutions of KI, *even in an inert atmosphere*. Thus in experiment 7 the iodine which makes its appearance on heating, soon distils off and leaves a colourless liquid in the distilling flask; if now the distillation be long-continued till the residue becomes concentrated, the latter again shows the presence of free iodine, which, on account of the increased concentration of the KIAq it is impossible to boil off. This observation is not founded solely on experiment 7, which is merely an example from other similar experiments.

* See Sutton's "Volumetric Analysis," Fresenius's "Quantitative Analysis," Thorpe's "Quantitative Analysis," &c.

† I have before shown (*Proc. Chem. Soc.*, No. 61, 1888—1889) that fairly strong solutions of cupric iodide—currently regarded as non-existent—can be obtained. These solutions are very unstable, and behave just as dilute solutions of free iodine.

TABLE I.

	C.c. KI solution.	C.c. FeI_2 solution.	C.c. HClAq.	C.c. H_2O.	Digestion. Drops Thiosulph.	Digestion. Remarks.	Distillation (see further on). Drops Thiosulph.	Distillation (see further on). Remarks.
1.	5	—	—	15	0	½ hour at 60°.		
2.	5	—	1	14	1	" "	0	
3.	5	—	5	10	3	" "	<1	
4.	5	—	5	10	11	½ hour at 60°.		
5.	5	—	1	14	8	½ hour at 60°, then allowed to stand 2¾ hrs.		
6.	5	—	5	10	22			
7.	15	—	5	—	15	½ hour at 60°.	2	The residue became colourless, then on further concentration again became coloured.
8.	5	—	5	10	<1	½ hour at 60°, but in atmosphere of CO_2.		
9.	15	—	5	—	<1	" "		
10.	5	5	5	5	4	½ hour at 60°.		
11.	—	5	5	10	2	" "		
12.	—	10	5	5	3	" "	<1	

The measurement of the thiosulphate solution was effected by an easily improvised "stillimeter," on the principle of Mariotte's bottle; it consisted of a *small* glass lime tower (as used in preparation of NH_3) fitted with tubes as represented in the diagram. The efflux tube, *b*, consists of a quill tube drawn fine at its extremity and bent three times at right-angles, as figured. A tube of this kind, whose point of efflux is above the level *d*, works more satisfactorily than efflux tubes not fulfilling this condition. The size of the drop as well as the drop-rate, is a function of the height *a d*; the size of the drop is also independent of the effective aperture of the tube *g*, *i.e.*, is independent of the precise opening of the tap, T.

The accuracy of such an apparatus is attested by the the following numbers, which show the weight of 30 drop portions delivered under varying conditions:—

1st Series, showing Dependence of Drop-weight on Level of *a*.

(α) Low level of *a*. .. 11·086, 11·087, 11·086, 11·087

(β) Higher level of *a*.. 11·118, 11·1185, 11·1185, 11·118

2nd Series, showing that Drop-weight is Independent of Effective Aperture of Tube *g*.

(α) Tap T *fully* open.. 11·0935, 11·094

(β) Tap T *just* open .. 11·094, 11·094

Using such an apparatus and very dilute standard solutions for the completion of any reaction, volumetric analyses may apparently be carried do a very high degree of accuracy. If the apparatus be used with a dilute solution for thus merely *completing* a reaction, its delivery should be tested against the stronger solution (used in the burette) every time the apparatus is filled.

It would seem almost impossible to obtain constant drops from a burette; we can never ensure that the tap is always opened to the same extent, and further, the effective pressure is always diminishing. The inconstancy of the following numbers (for the weight of 30 drops), obtained with one of Geissler's burettes, contrasts strongly with the constancy observed in the above experiments.

11·6325 } burette full.

11·5840, 11·5380, 11·6020, 11·6030, 11·5960 } burette about half full.

11·598, 11·626 } burette nearly empty.

It occurred to me that a choice between the two equations I. and II. might be made by investigating the actual amount of KI necessary to completely decompose a given mass of $FeCl_3$ under conditions admitting of a "complete" change. A ferric chloride solution was made in the ordinary way by solution of piano wire in HCl and subsequent oxidation of the solution with chlorine. After boiling off the excess of chlorine the acidity of the solution was *diminished* by the addition of KOHAq, and the *still fairly acid* solution made up to known volume. It was held more exact to determine the strength of the solution gravimetrically by precipitation with NH_3Aq than by primarily weighing accurately the iron dissolved. The mean of two closely agreeing experiments gave the strength as 0·0999 grm. per 10 c.c. A standard solution of KI (dried at 150°) was so made that 5 c.c. of the iron solution required 10 c.c. of the iodide solution in order to satisfy the ratio Fe : KI.

The first set of experiments was made in the ordinary way with digestion-bottles. In all cases but the last F, the air in the bottle was displaced by a rapid stream of CO_2 before digestion.* The temperature of the bath employed was 60° C., and the duration of digestion twenty minutes in each case.

Table II.

	Ratio $\frac{\text{molecules KI}}{\text{atoms Fe}}$	C.c. thiosulphate used to react with liberated iodine.
A	1	14·2
B	2	17·9
C	3	18·35
D	3½	18·6
E	Very large but unmeasured	18·7
F	,,	19·55

The numbers given in the first three cases marked the first disappearance of the blue iodide of starch; on allowing the solutions to stand the phenomenon of "after blueing" (*nachblauung*) was observed. By alternately adding enough thiosulphate to destroy the slight blue colour and allowing to stand on the water-bath for some time a point was reached after which no after-blueing was observed. This limit was always reached after a sum total of 18·6 to 18·7 c c. thiosulphate had been added.

The conclusions to be drawn from these experiments is that the reaction between $FeCl_3Aq$ and KIAq is complete only when rather over three molecules KI have been used for each atom of iron.† This fact speaks strongly in favour of equation II. The reason why exactly three molecules KI fail to completely decompose one molecule $FeCl_3$ is not far to seek. Under the conditions of the experiment there is no removal from the sphere of action, and the change is on that account an "incomplete" one, *i.e.*, factors and products are alike represented in the final equilibrium. When an excess of one of the factors of the change is taken the reaction is rendered complete so far as the other factor is concerned. In this case we see that the excess of KI above the ratio 3KI : Fe necessary to completely decompose the ferric chloride is small.

It occurred to me that by experimenting under conditions admitting the removal of the volatile iodine from the sphere of action I should find that *exactly* three molecules KI would completely decompose one molecule $FeCl_3$. In this I was mistaken. The distilling apparatus used in the following experiments was made completely of glass as figured. This form of apparatus offers many advantages over those usually described. When occasion demands the delivery tube, which is ground to fit the flask, can be rapidly and easily disconnected without any fear of a back-flow from R. The shaded portions, *a a*, represent bindings of thick string to facilitate this disconnection. Moreover, this form of delivery-tube is very easily washed out. Special experiment showed that with this apparatus, and using in R 10 c.c. of a solution of KI containing 40 grms. per litre, the whole of the iodine librated in *a* was retained by R. It is best to support the flask on an asbestos card, in the middle of which a small hole is cut. The flask can thus be rapidly heated by a bare flame without fear of fracture (see discussion of Table I.)

The experimental results are appended in Table III.

The results of these experiments (in which it is to be noted that the KI used to absorb the iodine was not measured in each case) are very irregular, and, on the whole, lead to the conclusion that in distillation one molecule KI serves to completely decompose one mole-

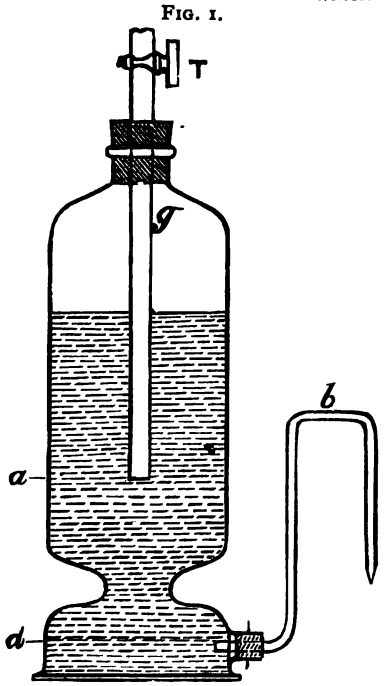
* I find, on reference to Mohr's "Titrirmethode," that he recommends the addition of a few lumps of acid carbonate of sodium to the digestion-bottle before heating. Experience, however, has taught me to favour extrinsically generated CO_2.

† Braun (*Zeit. f. An. Chem.*, 1864, iii, p. 453) regards 0·5 to 1 grm. KI sufficient for 1 grm. Fe in the form of ferric chloride; from the above experiments it appears that each grm. Fe requires about 3·5 grms. KI.

TABLE III.

	Ratio $\frac{\text{molecules KI}}{\text{atoms Fe}}$	C.c. thiosulphate required.	Remarks.
A ..	Just over 1.	14·9	In all these cases the residues in *a* were quite colourless. The values here given are in each case means of somewhat irregular results.
B ..	2	15·55	
C ..	3	14·6	
D ..	3½	14·45	
E ..	Very large but unmeasured.	—	The residue in A in this case did not become iodine-free, even on re-distilling twice with excess of water.

FIG. 1.



cule $FeCl_3$. At first sight, then, these distillation experiments would seem to support equation I., but I will show later on that they are by no means incompatible with the more rational equation II., supported in its turn by eqn. I.

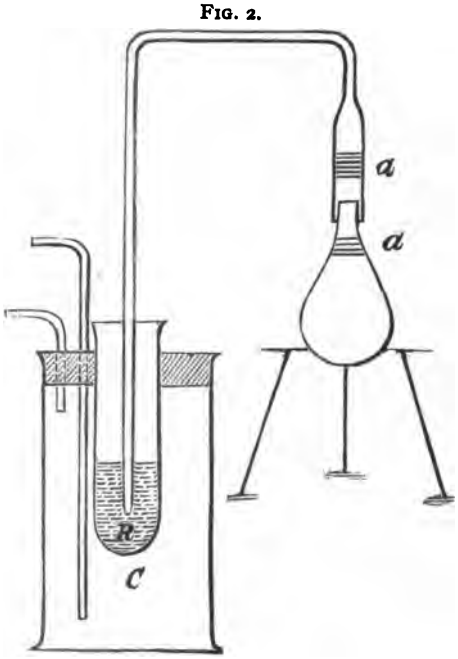
The mean of these results gives 14·7 c.c. thiosulphate as marking the limit of the action; whereas the digestion method gave 18.7 c.c. thiosulphate for the same limit. The thiosulphate was now standardised in the ordinary way against pure iodine, and it was found that (1) 16·3, (2)16·4 c.c. was the quantity theoretically necessary for the iodine liberated from KI by 5 c.c. of the $FeCl_3Aq$, the quantity always used in these experiments.

I subsequently found that the cause of these discrepancies was the presence of an impurity in the "puriss." potassium iodide used. It is well known that commercial KI frequently contains KOH and K_2CO_3; but this impurity is apparently not confined to the commercial article, for samples of the purest KI supplied by two of the best known British firms contained respectively 2·2 per cent and 1·9 per cent.* Now the extreme importance of this impurity in connection with iodometry in all its bearings has never, I think, been sufficiently emphasized; the text-books, in the fervour of their warnings with respect to the evils arising from the presence of iodate in potassium iodide, have completely overlooked quite as formidable an impurity. Both KOH and K_2CO_3 "fix" free iodine, and it therefore follows that all iodometric estimations (even the simple standardisation of thiosulphate against pure iodine dissolved in KI), unless special precautions have been taken to the contrary, are vitiated in varying degree by the alkalinity of the impure KI.

In the light of this revelation I now undertook a new series of experiments, with most satisfactory results, applying to the case in hand a fact worked out by Fresenius, viz.: that acid carbonates of the alkali metals have no action on iodine.

Fifty grms. KI were dissolved in 200 c.c. water, and the solution supersaturated with CO_2; 10 c.c. of the resulting solution were used to catch the liberated iodine in each of the following distillation experiments. A fresh

FIG. 2.



R, tube containing concentrated solution KI.
C, condensing apparatus.

thiosulphate solution was used in these later experiments; hence it became necessary to repeat the digestion-experiments, which otherwise would have been unnecessary, as the standard KI solution used was always thoroughly saturated with CO_2 (see *ante*).

TABLE IV

Distillation.

Ratio $\frac{\text{mols. KI}}{\text{atoms Fe}}$	C.c. thiosulphate sol.	Remarks.
1½	(α) 17·2 (β) 17·3 (γ) 17·3	
3	(α) 17·3 (β) 17·3	
Very large, but unmeasured.	17·3	In this case the residue never became iodine-free; consequently the residue and distillate were mixed and titrated together.

* A sample of Schuchardt's pot. iodatum puriss. was obtained and was found to contain only the *merest trace* of free alkali.

In all these cases the measured amount of the standard KI solution was first introduced into the distilling flask, then CO_2 passed through to saturation, and finally the iron solution was added. I am firmly convinced that the distillation method is much more rapid and workable than the digestion method.

TABLE V.

Digestion.

Ratio $\frac{\text{mols. KI}}{\text{atoms Fe}}$	C.c. thiosulphate used.	Remarks.
$1\frac{1}{2}$	17·25	
$4\frac{1}{2}$	17·4	
Very large, but unmeasured	17·3	In this case the colour of iodide of starch first disappeared at 15·8 c.c. thio.; then the phenomenon of *nach blauung* presented itself till the thio. titre reached the limit 17·3.

A direct determination of the iodine-titre of the thiosulphate solution (using the carbonated KIAq for the solution of the iodine) gave 1 c.c. thio. = 0·00655 grms. iodine. Of such a solution theory demands 17·26 c.c. for the iodine liberated by the amount of iron contained in 5 c.c. of the $FeCl_3Aq$ used. As is seen the theoretical demand is well satisfied by the experimental result.

The necessity of titrating the thiosulphate solution in kind (*i.e.*, against a ferric chloride solution of known strength), has always been urged in the papers on Duflos's reaction; but by giving heed to the precautions here indicated such a procedure is unnecessary. In short, the reaction between $FeCl_3Aq$ and KIAq is removed from the category of those "chemical equations which, though right enough as such, are only *approximately correct* as theories of the processes of titration."

The fact that the ratio* KI : Fe suffices for a complete reaction by the distillation method does not in the least incline me to favour equation I. as a representation of the *modus* of the change. I would explain what takes place, in terms of equation II., as follows:—

$$FeCl_3 + KI = (\alpha)\ \tfrac{1}{3}FeI_3 + KCl + \tfrac{2}{3}FeCl_3.$$

The $\frac{1}{3}$ FeI_3 at the high temperature of the experiment is completely resolved into $\frac{1}{3}$ FeI_2 + $\frac{1}{3}$ I, which latter is removed from sphere of action, rendering stage (α) complete. The second stage in the equation may therefore be represented:—

$$(\beta)\ \tfrac{1}{3}FeI_2 + KCl + \tfrac{2}{3}FeCl_3 + \tfrac{1}{3}I$$

Now, in a previous paper I have shown that solutions of $FeCl_3$ behave towards certain other substances practically as if they contained free chlorine. Re-arranging β in accordance with this view we get—

$$(\gamma)\ \tfrac{1}{3}FeI_2 + KCl + \tfrac{2}{3}FeCl_2 + \tfrac{1}{3}Cl_2 + \tfrac{1}{3}I.$$

This loose chlorine of the ferric salt now decomposes the ferrous iodide as follows:—

$$(\delta)\ \tfrac{1}{3}FeCl_2 + \tfrac{1}{3}I_2 + KCl + \tfrac{2}{3}FeCl_2 + \tfrac{1}{3}I$$

or, re-arranging,—

$$(\varepsilon)\ FeCl_2 + I + KCl.$$

It appears, therefore, that the final composition of the residue in this particular case is identical with that demanded by equation I., but that this final state is arrived at through the primary operation of Duflos's equation II.

* The fact that apparently rather more than 1 molecule KI per molecule $FeCl_3$ was required for completion of the change (*vide* Table III. A) is to be ascribed to the presence of impurity (K_2O) in the iodide weighed to make the standard solution used in this set of experiments. Experiments with KI freed from alkali by Grove's method showed that under these conditions 1 molecule KI serves to completely decompose 1 molecule $FeCl_3$.

The various stages when the ratio 2KI : Fe is employed may be similarly represented.

$$FeCl_3 + 2KI = (\alpha)\ \tfrac{2}{3}FeI_3 + 2KCl + \tfrac{1}{3}FeCl_3$$
$$(\beta)\quad \tfrac{2}{3}FeI_2 + \tfrac{2}{3}I + 2KCl + \tfrac{1}{3}FeCl_3$$
$$(\gamma)\ \tfrac{1}{3}FeI_2 + \tfrac{1}{3}FeI_2 + \tfrac{2}{3}I + 2KCl + \tfrac{1}{3}Cl_2 + \tfrac{1}{3}FeCl_2$$
$$(\delta)\ \tfrac{1}{3}FeI_2 + \tfrac{1}{3}FeCl_2 + \tfrac{2}{3}I + 2KCl + \tfrac{1}{3}I_2 + \tfrac{1}{3}FeCl_2$$

or, re-arranging,—

$$(\varepsilon)\ \tfrac{1}{3}FeI_2 + \tfrac{1}{3}FeCl_2 + I + 2KCl.$$

When the ratio nKI : Fe is used, where n = or > 3, the equation is as follows:—

$$FeCl_3 + n\text{KI} = FeI_3 + 3KCl + (n-3)KI$$
$$= FeI_2 + I + 3KCl + (n-3)KI.$$

It is obvious that in order to substantiate these views dilute solutions of $FeCl_3$ should have the power of reacting with dilute solutions of FeI_2, and such is the case.

A mixture of 5 c.c. FeI_2Aq (containing about 0·1 grm. Fe) with 30 c.c. water, and 5 c.c. of the standard $FeCl_3$ solution showed the presence of much free iodine, even in the cold, and in an inert atmosphere of CO_2.

A mixture of 1·7 c.c. FeI_2Aq, 3·4 c.c. $FeCl_3Aq$, and 35 c.c. water, corresponding to stage β of the equation representing the reaction with the ratio KI : Fe, behaved similarly.

In the light of these facts the cause of the "after-bluing" in the digestion experiments, which *only* appeared when less than about 3½ molecules KI per molecule $FeCl_3$ was used, is apparent. An equilibrium exists between $FeCl_2Aq$, FeI_2Aq, IAq (FeI_3Aq), $FeCl_3Aq$, and KIAq. On adding thiosulphate to decolouration this equilibrium is destroyed by the change of free iodine into sodium iodide. Slowly at low temperatures, more quickly at high ones, the NaI formed, reinforcing the small residual amount of KI, decomposes some of the residual $FeCl_3$, forming a new equilibrium, which in turn is again similarly affected by a fresh addition of thiosulphate, and so on till no more $FeCl_3$ remains unchanged. This "after-bluing" can, in accordance with the above explanation, be readily imitated by adding thiosulphate slowly to $FeCl_3Aq$ containing a little iodine and starch solution. Under these conditions we get the blue colour of iodide of starch coming and going just as in the above experiments.

This paper would be incomplete without an expression of the thanks I owe to Mr. Pattison Muir, in whose laboratory the work detailed was carried out, and to whose kind help I am a large debtor.

Gonville and Caius College Laboratory,
Cambridge.

A NEW PROCESS FOR THE VOLUMETRIC DETERMINATION OF SILVER, MERCURY, AND THALLIUM BY MEANS OF POTASSIUM IODIDE.

By ADOLPHE CARNOT

CHEMISTS possess excellent volumetric methods for the determination of silver, and also some, much less accurate, for the estimation of mercury. The author proposes a new method applicable to both these metals with almost equal correctness. It is founded upon the insolubility of silver and mercury iodides in a nitric solution, provided that such solution contains no alkaline iodide. The potassium iodide employed as a reagent is poured little by little into the acid solution until the starch used as an indicator is coloured by the iodine. The liberation of the iodine is due to the presence of a very strong proportion of nitric acid, in preference such as contain nitrous products, like that which has been exposed for some time to the light in a bottle. The silver or mercury iodide may be collected and weighed, but it is preferable to

use the reagent as a standard solution, and to measure the volume of liquid necessary for precipitation.

I. First take the case of mercury, which must be in the mercuric state. The solution diluted with water to 100 or 150 c.c. is put in a beaker with about 10 c.c. of nitric acid and a little clear starch paste. Then a decinormal solution of potassium iodide (16·61 grms. of the pure salt per litre) is dropped in from a burette, stirring continually with a glass rod. Each drop produces at first a yellow precipitate, which quickly dissolves on stirring; then the precipitate turns gradually to red. At the moment when the mercury is entirely converted into the insoluble iodide the least excess of the reagent liberates iodine, which at once colours the starch.

Before the end of the operation we perceive, at the place where the drops of the reagent fall, blue and afterwards brown spots, which disappear at first rapidly, then they form trains of a dark brown in the midst of the red liquid, and finally give it a general brownish tint. The exact moment must be seized when a permanent change of colour is observed. If this is ever so little overstepped, the liquid, when left to itself, remains of a blue colour after the subsidence of the red precipitate.

When the quantity of mercury to be determined has been approximately found by a first operation, it is advantageous to add at once almost the total quantity of the reagent necessary, and to add the starch and the nitric acid afterwards. The remainder of the standard reagent is then added drop by drop until the reaction is completed.

Synthetic experiments on quantities of mercury varying from 0·002 grm. and 0·100 grm. have given results as satisfactory as possible, leaving uncertainty only as to the tenths of a m.grm. The method is not suitable in presence of free hydrochloric acid or of alkaline chlorides, conditions which must be kept in mind in preparing the solution to be operated upon.

II. Silver is determined in the same manner as mercury. If the substance in question is of unknown composition we make first an approximate determination.

According to this first datum we calculate the approximate weight of the silver contained in the portion taken for analysis, we dissolve it in nitric acid, dilute it to 100 c.c., introduce the calculated quantity of the decinormal potassium iodide, and stir briskly so as to collect the pale yellow precipitate of silver iodide in the form of dense clots. We decant the liquid along with a little washing-water into a beaker, add some c.c. of starch paste, and about 10 c.c. of nitric acid slightly nitrous. If at this moment the liquid becomes blue it is exactly decolourised by means of a centinormal solution of silver nitrate (1·7 grms. nitrate per litre). If it is not coloured blue we pour in at first potassium iodide until the permanent blue tint appears, which is then removed again by means of the centinormal silver solution.

In this manner the author has obtained results accurate to 0·1 or 0·2 m.grm. when operating upon known quantities of silver, from 1 to 200 m.grms.

This process, in certain points, resembles that of Pisani, described in the *Annales des Mines*, founded upon the decolouration of silver nitrate by starch iodide prepared in advance in a standard solution. But the potassium iodide employed does not give rise, like Pisani's free iodine process, to the formation of silver hypoiodite, a cause of uncertainty in the volumetric determination of silver if the metal is in rather large quantities.

III. Thallium, which forms in a nitric solution a yellow iodide a little less insoluble than those of silver and mercury, may be determined by the same method, though with a little less accuracy.

Palladium gives rise to similar reactions, but its iodide is of so deep a colour that it is not possible to seize the exact moment when the free iodine begins to colour the starch. The process is, therefore, not applicable to its determination by this method.—*Comptes Rendus* (cix., p. 177).

NOTE ON THE

ANALYSIS OF CONCENTRATED SUPERPHOSPHATE.

By JOHN HUGHES, F.C.S., F.I.C.

Concentrated superphosphate containing from 37 to 41 per cent of phosphoric acid soluble in water usually contains in addition from 4 to 5 per cent of phosphoric acid, which is combined with oxide of iron and alumina in the form of precipitated phosphate.

This precipitated or reduced phosphate, correctly speaking, is *not soluble* in water, but is *soluble* in a concentrated solution of the superphosphate. Therefore, in extracting the ordinary soluble phosphoric acid in such superphosphates, or indeed in any superphosphate made from materials containing much iron and alumina, it is most important to take care that sufficient water is added for the *first extraction*, otherwise the soluble phosphoric acid is returned 1 to 2 per cent too high. In other words, the less water used for the *first* extraction the higher the percentage of soluble phosphoric acid reported.

The following two experiments are sufficient to demonstrate the practical importance of attention to the quantity of water employed:—

	No. 1.	No. 2
Percentage of phosphoric anhydride ..	37·95	39·60
Equal to tribasic phosphate of lime rendered soluble by acid	82·85	86·44

In No. 1 experiment 1½ grms. of superphosphate were placed in a small beaker and a little water added to soften the mass and allow of breaking up all lumps, the volume of the solution being then increased with cold water to 90 c.c., allowed to stand five minutes, and then the supernatant liquor filtered off. To the residue another 90 c.c. of cold water was then added, the whole carefully stirred, allowed to settle, and filtered as before. Finally the residue, with about 60 c.c. of water, was warmed gently, and the whole brought upon the filter and washed once with hot water.

In the filtrate the soluble phosphoric anhydride was determined by the magnesia method with the usual precautions.

In No. 2 experiment 3 grms. of superphosphate were taken and the mass broken up as in No. 1, but only 30 c.c. of cold water added for the first extraction. After standing, the clear liquid was filtered off and another 30 c.c. of water added for second extraction, then 60 c.c. for third, and 90 c.c. for fourth extraction, the residue being finally warmed up with boiling water and brought on the filter as in the case of No. 1, the total volume of liquid being the same in each experiment. In No. 2, as the the third and fourth washings came into the filtrate, the precipitate of phosphate of iron and alumina became apparent as the filtrate became diluted, whereas in No. 1 (which represents the process employed by the writer in all analyses of superphosphate) this precipitate is formed in the original solution and is collected on the filter with other insoluble phosphates.

It will be seen from the above results that, by omitting to take the precaution of adding sufficient water to the first extraction, phosphoric acid equal to 3½ of ordinary soluble phosphate of lime passes into the filtrate in the form of phosphate of iron and alumina, and becomes included with the phosphoric acid *soluble* in water, whereas it really exists in a form *insoluble* in pure water.

At the present time, when a considerable quantity of this concentrated superphosphate is being purchased and numerous analyses are being made, the author believes it will be useful to point out the probable cause of the differences between the analytical results of duplicate samples of this quality of superphosphate.

Analytical Laboratory,
79, Mark Lane, E.C., Aug. 12 1889.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

(Continued from p. 84).

Imports of Diamonds.—From the Custom import lists we find that after deducting the approximate value of cut stones other than the diamond, we find that import duty was paid on about 90,000,000 dollars worth of cut diamonds in the last twenty-one years; of these 68,000,000 dollars worth were imported during the last ten years. In 1868 1,000,000 dollars worth were imported, and 1,200,000 dollars worth in 1867, but about 10,000,000 dollars worth in 1887, or ten times as many as twenty years ago, showing the increase of wealth and the great popularity of the diamond among Americans, the above being the wholesale import figures. A single firm sells more than the entire imports of twenty years ago.

Diamond dust worth 464,905 dollars has been imported since 1878, 289,430 dollars worth from 1868 to 1878, and in 1869 to 1871 only 228 dollars worth; whereas with the opening of the Kimberley mines 80,707 dollars worth were imported the first year, showing what great benefit the arts received from the opening of the African diamond mines.

In 1878 the importations of uncut diamonds amounted to 63,270 dollars; in 1887 to 262,357 dollars; the total for the decade was 2,728,214 dollars, while in 1883 there were imported 443,996 dollars worth, showing that although we are cutting four times as many diamonds as we were in 1878, yet the importations have been falling off. This is partly because in the years from 1882 to 1885 a number of our jewellers opened diamond cutting establishments, but have either given up the business or sold out to others; for, in spite of the protective duty of 10 per cent on cut stones, cutting cannot be profitably carried on here on a scale large enough to enable one of the partners to reside in London, the great market for rough diamonds, to take advantage of every fluctuation in the market, and purchase large parcels which can be cut immediately and converted into cash; for nothing is bought and sold on a closer margin than rough diamonds.

Diamond Cutting.—The recent death of Mr. Henry D. Morse, of Boston, known as the pioneer diamond cutter of the United States, brings to mind many interesting reminiscences. He has scarcely received the credit he deserved for his work. That he was the first in this country to cut diamonds is well known, and the best cutters in the United States to-day received their training under him. But educating young Americans, both men and women, to his art, was not his greatest work. He showed the world that the art which had so long been monopolised by the Hollanders, was degenerating in their hands into a mere mechanical trade. His treatment of the diamond has given a great stimulus to the industry both in the United States and abroad. Shops were opened here and in London in consequence of his success. He was one of the few who studied the diamond scientifically, and he taught his pupils that mathematical precision in cutting greatly enhances the beauty and consequently the value of the gem. His artistic eye, sound judgment, and keen perception enabled him to carry the art nearer to perfection than is often attained.

It was in his shop that a machine for cutting diamonds was invented which did away in great measure with the tediousness and inaccuracy of the old manual process. Thanks to his labours, we now have among us the best cutters in the world—men who can treat the diamond as it should be treated to develop its greatest beauty. The fact that so many fine stones were re-cut here after he started his wheel led to a great improvement abroad in cutting, especially in the French Jura, and in Switzerland, where both sexes are now employed at the trade; and, as a result, the diamonds sold to-day are decidedly better than those of twenty years ago, before Mr. Morse turned his attention to the work. He, above all others, has shown us that diamond cutting is properly an art and not an industry.

There are at present about 12 cutting establishments in this country, employing from 1 to 50 men each, and in all about 100, at salaries ranging from 20 to 50 dollars per week. Most of the cutting done here is of a high class, some shops being almost entirely employed in re-cutting stones previously cut abroad. Ten years ago nearly all the diamonds used in the United States were purchased through brokers or importers. To-day, owing to the marvellous growth of the diamond business here, and the facilities for transatlantic travel, many of the large retail houses buy their diamonds direct in the European markets; and some have even established branches or agencies abroad.

In 1877 an international syndicate, composed of London, Paris, and Amsterdam jewellers, wishing to establish a uniform value for the carat, confirmed 205 m.grms. as the standard, and this has been pretty generally used abroad. Recently the discussion of the question has been re-opened, and it will probably end in the general adoption of the above standard in place of the twenty or thirty conflicting systems now in use in different parts of the world.

Twenty years ago the wholesale diamond merchants of Amsterdam did not exceed eight in number; but the development of the African mines has given so great an impetus to the trade, that within the past decade several diamond exchanges, or clubs, have been established as head-quarters for the transaction of business; one of these, the "Handelsbond," has a membership of 800 and owns a fine building, the rooms of which are so arranged with respect to light as to render deception difficult and to facilitate the sale of diamonds. Others, known as the "Golconda," and the "Koh-i-noor," are generally thronged with brokers and merchants, as also are the neighbouring coffee houses.

At present there are between 50 and 60 large diamond polishing establishments, employing perhaps 3500 polishers, who, however, no longer receive the princely wages of from 80 to 200 dollars per week which they received when the African mines first began to produce so largely, and much higher prices were paid for products of the second and third quality. When fortune smiled on them the cutters lived in luxury; to-day they only receive 15 to 40 dollars a week, and some even less than the former figure. To day every establishment does its own selling. It will doubtless be eventually a question of the survival of the fittest, and the entire cutting will be controlled by a few powerful firms.

Sapphire.—In 1882 a very remarkable discovery of sapphire was made in the Zanskar range of the north-western Cashmere Himalaya, near the line of perpetual snow, a short distance from the villege of Machel, and one-half day's journey from the top of Umasi Pass. The stones were found at the foot of a precipice, where a landslide had taken place, the including rocks being gneiss and mica.

At first they were merely collected by the villagers, who were attracted by the beautiful colours; and so little was their value realised that they were used as flints for striking fire with steel. They were so abundant at first that one writer speaks of having seen about a hundredweight of them in the possession of a single native. Traders, however, soon carried them to the distant commercial centres, where their value became known. There was an instant rush of jewellers' agents to the locality of the mine, and the price rose rapidly until about £20 per ounce was paid for good specimens, at which rate they have remained. The Maharajah of Cashmere promptly exercised his authority and sent a regiment of sepoys to take possession of the mines and harry the natives who were suspected of having stones in their possession or any knowledge of new localities where the

* Abstract from "Mineral Resources of the United States."

gems could be found. Any one they laid hands on who had money was suspected either of having sold sapphires or being about to purchase them, and was despoiled, or even imprisoned. This naturally enough had the effect of compelling secrecy. Several crystals were found weighing from 100 to 300 carats each. During the first year of the discovery the Delhi jewellers are said to have bought up more than £20,000 worth of these sapphires. Exceptionally fine sapphires to-day bring from 65 dols. per carat to 125 dols., which is less than before this great find.

The acquisition of the Burmese ruby mines cost the British Government a vast sum of money. On the wars of 1826 and 1852 England expended 75,000,000 dollars and 15,000,000 dollars, respectively, and after all this sacrifice of treasure the Burmah and Bombay Trading Company claimed, four years ago, that King Thebaw, of Burmah, had arbitrarily cancelled the leases by which the company controlled the output of the ruby mines near Mandalay. A meeting was accordingly held at Rangoon, on October 11, 1884, presided over by Mr. J. Thompson, agent for Messrs. Gillanders, Arbuthnot, and Co. The result was the war of 1886, which involved the raising of an army of 30,000 men and an outlay of 5,000,000 dollars, but the British Government gained control of the long coveted ruby mines. The question which next presented itself was, how should they be worked? Several firms were desirous of securing the lease, and after the Indian Government had virtually closed a lease to Messrs. Streeter and Co., the London jewellers, at an annual rental of 4 lakhs of rupees (£40,000), for a term of five and one-half years, with the privilege of collecting 30 per cent on all stones mined by others, the Home Government revoked the lease for some unexplained reason, probably on account of trade jealousies, although Mr. Streeter had apparently every assurance of the acceptance of his proposition, and had even made preparations to begin work at the mines.

The ruby mines of Burmah are situated in the valley of the Mogok, 51 miles from the bank of the Irrawaddy river, and about 75 miles north of Mandalay, at an altitude of 4200 feet. Concerning these mines very little has been learned up to the present, as they were always the monopoly of the Crown and were jealously guarded. It was said that they paid King Theebaw's Government annually 100,000 rupees, and one year 150,000 rupees. Mining is carried on there by forty or fifty wealthy natives, who employ the poorer townspeople at liberal wages; but at present only seventy-eight mines or diggings are in operation, and the work is done in the most primitive manner. The gravel is carried in baskets. The holes from which they are taken are allowed to fill with water every night. All of the gems are sent to Ruby Hall, Mandalay, to be valued. At present the royalty exacted by the English Government is 30 per cent. A stone was lately sold in Mandalay for 8000 rupees, but without the knowledge of the officials.

One thing, at least, we learned from the British occupation of Burmah, namely, that King Thebaw did not own the dishes of rubies which were said to outrival anything known. His possessions of this kind proved to be only a few stones of poor quality.

(To be continued).

Fuel and its Applications.—Messrs. J. and A. Churchill hope to publish in September an important work on "Fuel and its Applications," by Mr. E. J. Mills, F.R.S., and Mr. F. J. Rowan. It will be the first volume of a large work on Chemical Technology, of which Mr. C. E. Groves, F.R.S., will be the general editor, and which will be founded on one written by Richardson and Ronalds, familiarly known as "Knapp's Technology." Messrs. Mills and Rowan's work on Fuel is in reality a new work, in which the applications of fuel to arts and manufactures, as introduced by the most modern discoveries, is given to the scientific world. The volume will be profusely illustrated.

A RAPID METHOD FOR THE REDUCTION OF FERRIC SULPHATE IN VOLUMETRIC ANALYSIS.*

By CLEMENS JONES, Hokendauqua, Pa.,
Chemist to the Thomas Iron Company.

The difficulties attending the reduction of ferric sulphate in the determination of metallic iron by the method of Marguerite are often serious, and affect time, patience, and accuracy. They depend upon the condition and purity of the zinc used, the state of saturation of the solution, acidity, and temperature.

D. J. Carnegie (Chem. News, lvii., No. 1481) says that ferric solutions are instaneously reduced by the use of zinc-dust. But there are obvious objections to its employment in quantitative work. Dr. Drown found that "a concentrated solution, not too acid, was reduced by five grms. of pulverised zinc in two or three minutes, without other heating than that due to the chemical action." But the zinc in excess of the stoichiometrical amount must be dissolved. This has been the main obstacle. Large excess of sulphuric acid, heat, or both, must then be employed; and either involves loss of both time and accuracy in the volumetric method.

Marguerite's method is, in point of celerity and refinement, the most scientific of all the "iron methods." If the iron solutions have been properly prepared the end-reaction is sharper and more quickly obtained than by any other. There is no loss in testing for final oxidation, as potassic permanganate is its own indicator. Besides, the permanganate solution can be most quickly prepared and accurately standardised.

Hence there is a natural preference for this method in determining metallic iron. It permits direct and rapid titration. Only facilitate the reduction of the ferric sulphate, and it is the most valuable of all methods, combining the utmost rapidity with the highest accuracy attainable.

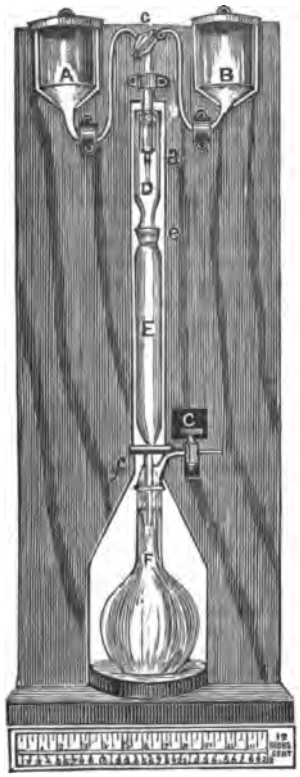
There is no difficulty in obtaining iron as ferric sulphate; but the reduction of this to the ferrous state has hindered the precision of the permanganate method. Discrepancies in results are all to be set down to the errors introduced in the reduction with zinc. The care to secure complete reduction—how frequently is it lost through the presence of a minute grain of zinc, washed down from the neck of a flask in titrating, and now derisively tossing up a little chain of hydrogen bubbles! Again, a very hot solution will decompose an excess of reagent. And, moreover, as I shall again remark, it is probable that the largest impurity in pulverised zinc is not iron, as heretofore supposed, but carbon.

The size of the particles of the pulverised zinc employed in the method which this paper describes is determined by passing through a 40-mesh upon a 60-mesh sieve.

Observing the action on zinc of ferric solution in sulphuric acid, I noticed that in all cases, with practically the same amount of acid and zinc, the latter dissolved more rapidly when the solution was more highly saturated with ferric salt; that the time for reduction, under the conditions mentioned, was dependent on the strength of the ferric solution. This was evidence that a sufficient number of zinc particles should be exposed in a proper ratio to the ferric salt; that each molecule takes the same time to reduce when unaffected by its unreduced neighbour, which is the time of contact; and that, therefore, were each molecule presented to new particles of zinc successively, reduction would be instantaneous. Filtering the ferric solution through pulverised zinc would then demonstrate this fact, which I found to be the case. *A solution of ferric sulphate is instaneously and completely reduced by filtering through pulverised zinc.*

* Read before the American Inst. Mining Engineers, New York Meeting, Feb., 1889.

The apparatus figured below was designed for the rapid reduction of ferric solutions. It consists of two cups,* A and B, of about 300 c.c. capacity, the outlets of which connect alternately, by means of a 3-way cock, C, into the joint-tube, D. This tube is provided with a packing space, *d*, which is filled with an asbestos roll kept in place by a ring of cork. The tube moves up and down freely. At its lower end *e*, it is ground to fit the detachable tube, E. This is for the pulverised zinc, and at its lower end has a stopper, *f*, ground to fit the titrating flask, F, of about 700 c.c. capacity. The stop-cock, G, connects with the vacuum-pump. The tube E is disconnected by pushing it up, grasping the neck of the flask with one hand, removing with the other the round block which supports the flask, and then detaching the flask F. The tube E now rests on the little shelf shown in the cut. This is drawn out, and frees the tube at its ground-joint, *e*.



Reductor, for the Reduction of Iron Solution by Filtration through Zinc.

A wad of fine glass wool, sufficiently thick to make a good filter, is inserted into the tube, and the pulverised zinc is filled over this for four-fifths the length of the tube. This holds about 300 grms., which is enough for 60 filtrations. The tube is then replaced by reversing the manner of removal, connection is made with the filter-pump, and the apparatus is ready for use. It is first necessary to wash the column of zinc with dilute sulphuric acid. This acid is made up of one part of acid of 1·84 sp. gr. to two parts of distilled water, and is used throughout in all work upon iron determinations. Of this about 30 c.c. is taken, transferred to the cup A, and diluted to 300 c.c. Stop-cock G is opened for suction, and then the three-way cock C is turned to discharge the cup A. A vacuum of 5 to 6 pounds or more, gauge-indication, must be used, since the large volume of disengaged hydrogen retards the filtration. The cup and the column of zinc are then washed free from acid by five rinsings. This operation is repeated four times, and is then finished for this tubeful of zinc.

Below is a series of trials, undertaken to determine the proper correction for iron in the zinc. Owing to the small amount of reagent required for the end-reaction, it was impossible to obtain a reading under 0·1 c.c., which, as will be seen further on, is too much for even so large a quantity of zinc.

No. of test.	Amount of $K_2Mn_2O_8$. C.c.
1	0·4
2	0·2
3	0·13
4	0·12
1	0·4
2	0·2
3	0·15
4	0·13
1	0·4
2	0·15
3	0·13
4	0·11
1	0·4
2	0·2
3	0·13
4	0·1

These were made at different times upon new quantities of zinc, and with solutions of $K_2Mn_2O_8$ of slightly varying strength. Beyond the fourth trial in each case it was impossible to get less than one drop of the reagent into the solution. This is nearly 0·1 c.c., and in every instance gave a strong colouration.*

Evidently the largest amount of iron in the zinc is only on the outside of the particles, as the quantity dissolved in the reductor is less than five grms. for each filtration. By the ordinary method of dissolving all the zinc, the correction is rarely below 0·15 c.c. for 5 grms.

Exactly the same procedure is adopted to reduce a ferric sulphate solution, except to use both cups A and B. After the first is emptied it is washed with cold water five times. This incidentally cools the column of zinc and retards unnecessary solution. The other cup is then connected by turning the 3-way cock C, and washed in like manner. In each case this suffices to free the apparatus from all traces of iron or sulphuric acid. G is then closed, the 3-way cock is turned again to relieve the pressure, and the flask is removed. Time for reduction, two minutes.

Solutions obtained in this way are beautifully clear and perfectly reduced. The volume and temperature are practically constant: the former being about 400 c.c., and the latter about 40° centigrade. Uniformity marks the entire process, and there is a minimum quantity of zinc sulphate. Dilute solutions must be used. There should be not over 50 c.c. sulphuric acid in 300 c.c. of the ferric solution ready for reduction.

An experiment was tried in reducing the solutions after oxidation, used in standardising the permanganate. Iron wire taken at 0·996 Fe.

Standardisation.

	Weight of wire. Grm.	$K_2Mn_2O_8$ C.c.	Reaction.	Factor.
No. 1.	0·1271	16·48	Tinged	1 c.c. = 0·007681 Fe
No. 2.	0·12175	15·78	Sharp	1 c.c. = 0·007684 Fe

Reduction of these Solutions.

	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.
No. 1	Complete	16·42	Tinged
No. 2	,,	15·8	Sharp

* I find this form of cup not so convenient as the bulb-shape of a separatory funnel of the same capacity.

* I have since obtained a reading down to 0·03 c.c. by closing the burette-tip.

This treatment applied to a hæmatite ore gave (No. 2963)—

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.	Iron. Per cent.
No. 1.	0·1527	Complete	7·2	Tinged	34·7207
No. 2.	0·1526	,,	7·2	Sharp	34·7441

(Reverted: filtered through the Reductor)—

No. 1	,,	7·2	Sharp
No. 2	,,	7·2	,,

Direct determination of metallic iron in the wire used in standardising gave the following results:—Weight of wire, 0·12405 grm. dissolved in sulphuric acid and oxidised. Reduced by filtration.

Reduction.	$K_2Mn_2O_8$ c.c.	Reaction.	Iron. Per cent.
Complete	16·07	Sharp	99·5420

Factor, 1 c.c. $K_2Mn_2O_8$ = 0·007684 Fe.

Solution again reduced by filtration. Reduction complete. $K_2Mn_2O_8$, 16·10 c.c., as compared with 16·07 in the former reduction. Difference, 0·03.

The *apparent* correction for iron in the zinc is the increase in last reading or 0·03 c.c. of the reagent. Time required to reduce and titrate this solution twice, *ten minutes*.

While the apparent correction is thus 0·03 c.c., it is inadvisable to use it as a constant, since the true correction can be applied for each case, and is really variable, depending upon acidity and degree of saturation.

In the following example, the test of hæmatite ore (No. 2922), carried through in duplicate, the ferric sulphate was first reduced by the usual method of adding the zinc to the solution, and then entirely dissolving it, and deducting 0·3 c.c. as the correction after titration. Each solution was then filtered through the Reductor, and on the supposition that for each treatment with zinc (on account of filtration) but 0·1 c.c. is to be deducted; the results are seen to be coincident. By "Reverted" is meant filtering through the Reductor. The value of 1 c.c. $K_2Mn_2O_8$ is 0·007678 Fe.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$.	Correction.	Iron. P.c.
No. 1	0·1360	Complete	7·4 sharp.	0·3 = 7·1	40·06
,,	Reverted	,,	7·3 ,,	0·2 = 7·1	= 40·06
No. 2	0·1379	,,	7·49 ,,	0·3 = 7·19	= 40·03
,,	Reverted	,,	7·39 ,,	0·2 = 7·19	= 40·03

Another (No. 2971), with a difficulty-fusible residue, was tried directly, each solution being reduced twice by filtration. Time for reducing and titrating in duplicate, twenty minutes.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.	Iron. Per cent.
No. 1	0·1505	Complete	9·27	Sharp	
2nd trial		,,	9·21	,,	= 47·0230
No. 2	0·1823	,,	11·29	,,	
2nd trial		,,	11·23	,,	= 46·9132

Assuming that for ordinary purposes the correction obtained by reverting the solution used to standardise the permanganate would be a safe one, I have applied it to the determination of iron in an ore, with the following results:—

Standardisation.

	Weight of wire. Grm.	$K_2Mn_2O_8$. C.c.	Reduction.	Correction. C.c.
No. 1.	0·11915	15·48		
	Reverted	15·55	Complete	0·07
No. 2.	0·1261	16·4		
,,	Reverted	16·44	,,	0·04

Factor, 1 c.c. $K_2Mn_2O_8$ = 0·007664 e.

Determination.

	No. 2997) Weight of ore, grm.	$K_2Mn_2O_8$. C.c.	Correction.		Iron. Per cent.
No. 1.	0·1576	9·58	0·07	9·51	46·246
No. 2.	0·2351	14·3	0·07	14·23	46·388

In like manner a rich hæmatite ore (No. 3066) gave:—

No.	Weight of ore. Grm.	Metallic iron. Per cent.
1.	0·2302	60·03
2.	0·1645	60·17

Theoretically a neutral, or nearly neutral, solution of ferric sulphate should be reduced by zinc in this way without dissolving the latter appreciably, at least, not to the extent of introducing the error due to its impurity. As nearly satisfying these conditions, by the use of a minimum of sulphuric acid, the two following examples afford a remarkable demonstration. The experiments were conducted like the foregoing:—

Factor 1 c.c. $K_2Mn_2O_8$ = 0·007656 Fe.

No. 1.

Weight of wire, 0·12085 grm.	Amount of $K_2Mn_2O_8$, c.c.
1st trial	15·72
2nd ,, ,, ...	15·78

No. 2.

Weight of wire, 0·11315 grm.	$K_2Mn_2O_8$, c.c.
1st trial	14·695
2nd ,, ...	14·695

Metallic iron 99·432 per cent.

There appears to be a deeply-rooted belief that iron is the only impurity in pulverised zinc which reduces the $K_2Mn_2O_8$; but I think the error is in all cases largely due to the carbonaceous residue. Five grms. of zinc were dissolved in sulphuric acid, and then found to require 0·13 c.c. of $K_2Mn_2O_8$. After oxidation, a test of the solution gave *no* colouration with potassium sulpho-cyanate. Oxidation with nitric acid gave a like result.

Twenty-five c.c. of sulphuric acid were diluted to 300 c.c. and passed through the reductor. $K_2Mn_2O_8$ required 0·05 c.c. One drop more was added, and the solution allowed to stand until clear. It was then tested with potassium sulpho-cyanate, and gave *no* colouration. A like experience followed in repeated trials of dissolving the zinc directly; but subsequent treatment of these solutions with ammonia and filtration gave evidence of iron. A determination of iron in the zinc used in these experiments gave the following:—5 grms. of zinc were dissolved in sulphuric acid. $K_2Mn_2O_8$ required 0·1 c.c. = 0·0154 per cent iron. As in the first case, 5 grms. were dissolved and the solution filtered through the reductor. $K_2Mn_2O_8$ required 0·12 c.c. Increase, 0·02 c.c., equivalent to 0·0030 per cent iron.

Mr. P. W. Shimer has since suggested to me the probability of lead existing in the black residue. This I have found to be the case.

Ignition of the residue leaves a small fused mass which, on dissolving in hydrochloric acid, reveals iron by the sulpho-cyanate. May not this residue be soluble under accidental conditions when exposed to the action of the solution for an hour or more by the old method of reduction? I have frequently noticed that it is perceptibly smaller in bulk. Again, if the solution is warm, may not final oxidation of the ferrous salt have an effect in dissolving it?

If it should prove to be a carbon compound, the reducing action on the $K_2Mn_2O_8$ would be increased beyond the correction for iron as ordinarily obtained. Filtration undoubtedly obviates these difficulties.

As touching this reducing action, the following experience may be cited:—An analysis in duplicate by the old method gave an unaccountable difference in results. The one solution, with the high result, was noticed to have a

dark colour and lustre. Subsequently this proved to be due to a very finely divided sediment, apparently carbon.

(No. 2978)	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1. ..	0·2174	Complete	11·75	0·3	40·47
No. 2. ..	0·1795	,,	11·12	0·3	46·31
No. 2. ..	Reverted	,,	9·61	0·15	40·49

Factor, 1 c.c. $K_2Mn_2O_8$=0·007684 Fe.

Here is another similar case:—

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1. ..	0·1951	Complete	16·95	0·18	65·80
No. 2. ..	0·1928	,,	15·6	0·18	60·92
No. 1. ..	Reverted	,,	15·9	0·3	61·21

Factor, 1 c.c. $K_2Mn_2O_8$=0·007656 Fe.

The following test of an ore is added as an illustration of the capability of this method for rapid reduction. 1 c.c.=0·007671 Fe.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1. ..	0·1566	Complete	13·35	0·05	65·1496
No. 2. ..	0·1820	,,	15·51	0·05	65·1569

Time required to reduce and titrate in duplicate, twenty minutes.

The investigation of this principle of reduction, which I believe to be new, has been governed by the time afforded in the few and brief intervals of regular technical work. I think the method capable of still further advancement and application. At the present stage of the enquiry, it presents the most rapid and accurate treatment for the estimation of iron.

The apparatus was made by Emil Greiner, 63, Maiden Lane, New York, whose intelligent and skilful workmanship has been of great service to me.

NOTICES OF BOOKS.

The Stevens Institute of Technology, Hoboken, New Jersey. Exterior and Interior Views by the Phototype Process, from Negatives by Prof. W. H. Bristol, M.E.

This work affords a two-fold interest. On the one hand, it gives us a brief view of the past history and the present condition of the Stevens Institute. On the other hand, it is important as illustrating the vast progress of photographic art.

The Stevens Institute owes its origin to private munificence. In 1867 the late Mr. E. A. Stevens bequeathed a suitable site and the sum of 150,000 dollars for the erection of a building "suitable for the uses of an institute of learning," and also, as an endowment for such institution, any sum, not exceeding 500,000 dollars, which his executors might think necessary. The executors considered the whole of this sum necessary, and appropriated it accordingly. But, on both sides of the Atlantic, there is many a slip between the cup and the lip. The Government of the United States demanded, and seized upon, 45,000 dols. as a "collateral inheritance tax," or, as we should say, legacy duty. Frequent attempts, we read, have been made to get this money returned, but without success—the more to be regretted as the Government of the United States seems to be suffering from a plethora of wealth. This transaction reminds us of the old evil days when Waterton, returning home with his splendid collections in natural history, a large part of which were destined for public institutions, found himself compelled to pay a tax of 20 per cent upon their supposed value.

In 1870 Prof. H. Morton, Ph.D., at that time occupying the Chair of Chemistry in the University of Pennsylvania, was appointed president, and a charter of incorporation was duly secured.

Chairs o fphysics, mathematics, chemistry, mechanical engineering, mechanical drawing, languages, and letters were at once instituted.

Chairs of experimental mechanics and shop-work, of marine engineering, of applied electricity, and of analytical chemistry have been subsequently added.

The photographs show the Front of the Institute Building, the East Side, the Institute Building looking east, the view through Castle Point Gateway, the rear of the Institute Buildings, the general views from the Institute looking eastwards and south-eastwards, the Gateway of Castle Point, Castle Point Homestead, the Old Lecture Hall, the Library, Physical Laboratory, the Engineering Lecture-room, the rooms for drawing looking eastwards, the Chemical Laboratory, the Work-shop looking north-eastwards, East Side of Work-shop, its West Side, the Foundry in Basement, the Mechanical Department in the East Basement, the Electrical Laboratory, the Electrical Lecture-room, the Electrical Gallery in Workshop, the Boat Engine of Colonel John Stevens (1804), the Stevens School, a preparatory institution, and the Entrance to the Stevens School. Some of these illustrations, as photographs, call for especial notice.

In the views of exteriors we notice that while the foregrounds are perfectly clear and distinct the distances have none of that heaviness so much complained of in photograph landscapes. This is particularly to be noticed in the view from the Institute looking to the east. Here the city and the open country in the back-ground gradually fade away in the distance, as in nature. In the view to the south-east the distance is also happily rendered. The view of the workshop looking north-eastwards shows a novel and ingenious method of overcoming a difficulty which may often present itself in photographing interiors. We find here a row of windows facing the observer, or the camera, whilst between them and the eye come in a multitude of dark objects, full of details, wheels, driving-bands, riggers, chains depending from pulleys, &c., yet there is no blurring or obscurity. This result is obtained, as President Morton informs us, by calling in the flash-light to the assistance of daylight. The windows were first covered with dark screens, and the camera was used with a small stop. Long exposures were given, and the "flash-light pistol" was used a number of times at the points which a previous negative had shown to be deficient in illumination. Then the lens was covered up, the screens were removed from the windows, and the camera was uncovered again for half a second. This useful expedient has been applied in some of the other interiors.

Some of the rooms are illuminated with glow-lamps, others with gas, and others seem to be fitted up for both these kinds of lighting.

Judging from these illustrations we should conclude that the Stevens Institute turns its attention much more to mechanical than to chemical technology. The chemical laboratory appears well organised for analysis and for research, but we see no workshops where the student may be initiated in the various branches of industrial chemistry. Perhaps if the Government of the United States sees its way to refund the 45,000 dollars this deficiency may be supplied.

Journal and Proceedings of the Royal Society of New South Wales. Sydney: The Society's House. London: Trübner and Co.

A paper on an "Improvement in Anemometers," by Mr. H. C. Russell, F.R.S., makes known the startling fact that the pressure of the wind in sudden gusts may amount to at least 95 lbs. per square foot. Australia is not, indeed, liable to the frequent tornados which inflict such damage

in the United States, but a gentleman who took part in the discussion on Mr. Russell's paper mentions a storm coming up from the southward which twisted the head off a gigantic tree, from three to four feet in diameter, the head, which must have weighed 200 tons, being suspended in the air before it fell to the ground.

A paper by J. H. Maiden, F.L.S., on "Indigenous Australian Forage Plants," enumerates a number of poisonous plants which occasion at times much damage to cattle. Some of the principles which they contain would form interesting subjects for chemical research.

A much dreaded plant is *Bulbine bulbosa*, the "Native Onion," a liliaceous plant, which is found in all the colonies except Western Australia. It proves fatal to sheep, horses, and cattle.

Castanospermum australe, the "Moreton Bay chesnut," or bogum of the aborigines, is found in Queensland and the northern portion of New South Wales. It is accused of destroying cattle, though the seeds when cooked are quite harmless to man.

Eumophila longifolia, the emu-bush, is remarkable as one of the first trees to be barked by rabbits.

Euphorbia Drummondi is almost invariably fatal to sheep. The head swells to an enormous extent, and becomes so heavy that the animal drags it along the ground.

Gastrolobium spp. are familiary known as poison bushes and render some tracts of country unoccupiable.

Swainsonia Greyana causes madness in horses. After eating it they "obstinately refuse to cross a small twig lying on the ground, imagining it to be a great log." Sometimes they endeavour to climb trees and commit other absurdities." Some alkaloid is probably present.

Mr. J. H. Maiden also contributes an important paper on Australian products containing tannin. Numbers of these materials contain proportions of tannin sufficient for use on the spot, *i.e.*, 13 to 14 per cent. A few are sufficient to be worth exportation, *e.g.*, *Acacia decuriens*, 36 per cent; *A. elata*, 20 per cent.; *Eugenia Smithii*, 28 per cent.

Considering the large production of hides in the colonies he considers it probable that the leather industries have a great future in Australia.

Prof. A. Liversedge, F.R.S., read a paper on "Some New South Wales Minerals." The "platinum" nodules found along the coast contain only about 30 per cent of platinum, and are made up chiefly of osmium and iridium.

Medals and money prizes are offered by the Society for the best original papers on—

The influence of the Australian climate in the development and modification of disease.

On the silver-ore deposits of New South Wales.

On the occurrence of precious stones in New South Wales, with a description of the deposits.

The papers must be sent in not later than May 1st, 1890.

The subjects for the succeeding year, to be sent in not later than May 1st, 1891, are—

The meteorology of Australia, New Zealand, and Tasmania.

The anatomy and life-history of the *Echidna* and the *Platypus*.

The microscopic structure of Australian rocks.

It must be noticed that no award will be made for a mere compilation. A memoir, to be successful, must be, in part at least, the result of original work on the part of the sender.

Analysis of Lead Peroxide.—L. Opificius.—The author dissolves lead peroxide or red lead by covering the sample with nitric acid of sp. gr. 1·2, and adding a slip of chemically pure metallic copper. Without the application of heat the lead peroxide is quickly dissolved if frequently stirred. The process has the advantage of dispensing with the use of organic reducing agents.—*Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 6, August 5, 1889.

Combination-heat of Fluorine and Hydrogen.—MM. Berthelot and Moissan.—When gaseous fluorine and hydrogen combine, forming gaseous hydrofluoric acid, the heat evolved = 37·6 cals. If the hydrofluoric acid is in solution the heat = 49·4 cals.

The Relations of Atmospheric Nitrogen with Arable Mould.—Th. Schlœsing.—The author mentions that Hellriegel and Wilfarth have proved that leguminous plants really fix gaseous nitrogen, requiring, however, the co-operation of certain microbia inhabiting vegetable mould. These organisms fix themselves on the rootlets, producing the tubercles well known to botanists. M. Schlœsing has, therefore, repeated his experiments to ascertain if the bare soil is capable of fixing nitrogen. The results have been constantly negative, not one sample being found which, when bare of vegetation, fixes gaseous nitrogen. Hence he concludes that such earths, if they exist, are exceptions upon which the farmer cannot reckon.

Study of the Electric Phenomena Produced by Solar Radiations.—Albert Nodon.—Solar radiations, if they encounter an insulated conductor (metal or carbon) communicate to it a positive charge. The magnitude of this charge increases with the intensity of the solar radiations, and decreases with the hygrometric state of the air. The phenomenon ceases if clouds pass before the sun. Solar radiations may be one of the causes of the electrisation of clouds.

Researches on the Sulphites.—P. J. Hartog.—The author has studied, chiefly from a thermo-chemical point of view, the normal double potassium and ammonium sulphite and the sodium-potassium sulphite-bisulphite.

The Combustion-heat of Some Organic Compounds.—J. Ossipoff.—A thermo-chemical study of the bisubstituted succinic acids.

Chemical and Thermic Study of the Phenolsulphuric Acids. Orthophenolsulphuric Acid.—S. Allain Le Canu.—The author lets fall, drop by drop, pure refrigerated sulphuric acid into pure phenol, kept at −10°, stirring, and letting the mixture slowly take the ordinary temperature, and keeping the vessel covered in order to exclude the moisture of the air. In about eight days all the phenol is dissolved and the mixture is poured slowly into water, avoiding any rise of temperature. The sulphuric acid remaining free is determined and got rid of by neutralising with barium carbonate. The barium sulphate is filtered off and the filtrate is neutralised with pure potassium hydrocarbonate.

On Camphor Monochlorised by Means of Hypochlorous Acid.—P. Cazeneuve.—This camphor is not chlorised in the methyl or propyl chains. Its slow decomposition by alcoholic potassa and the production of a chloro-nitro-derivative by the action of fuming nitric acid do not allow it to be considered as comparable to benzyl chloride.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

Wave-length of Spectral Lines of Metals in the Ultra-violet Portion of the Spectrum.—J. Trowbridge and W. C. Sabine (*Proceedings of American Academy of Science and Art*, per Chemical News).

Researches on Phenomena of Depression in Thermometers.—Memoirs have appeared by R. Weber, H. F. Wiebe, and A. Böttcher. The first-mentioned shows that the presence of alumina in the glass has in this respect no injurious influence.

General Law of Decrease of Volume during the Solution of Salts in Water.—A. Hentzsch (*Annalen der Physik und Chemie*).—No details are given.

Catalytic Action of Metals upon Detonating Gas and the Occlusion of Hydrogen.—A. Berliner.—The author regards occluded hydrogen as the cause of all the catalytic phenomena which he has observed (*Annalen der Physik*). Stephen Cooke has studied the reductive action of hydrogen in presence of platinum (*Glasgow Phil. Trans.*, per Chemical News).

Ultra-violet Spectral Lines of Nickel and Cobalt.—G. D. Liveing and J. Dewar.— *Proceedings Royal Society*.

Influence of Temperature upon Evaporation and Diffusion of Vapours.—A. Winkelmann (*Annalen der Physik und Chemie*).—No particulars are given.

Measurement of Rate of Efflux of Liquids from Narrow Apertures.—Th. Vautier (*Annales de Chimie et Physique*).—No particulars are given.

Prevention of Bumping during Boiling.—C. Tomlinson (Chemical News).

Determination of Melting-point in Oils Containing Soap.—W. F. K. Stock.—From the *Analyst*.

Spectral Apparatus.—Hugo Krüss.—For particulars the reader is referred to the *Zeitschrift fur Instrumentenkunde*.

Microspectrometer.—Th. W. Engelmann.—For construction the reader is referred to the *Zeitschrift fur Instrumentenkunde*.

A New Microscopic Lamp.—W. Kochs and Max Wolz.—The nature of this lamp cannot be understood without the two accompanying figures.

A Substitute for the Oil-Spot in Bunsen's Photometer.—O. Lummer and E. Brodhun.—For the description of this apparatus the reader is referred to the original.

Polarising Apparatus.—Steeg and Reuter.—Improvements on Steeg's polarising apparatus for the examination of wines.

Apparatus for Measuring and Dropping Small Quantities of Mercury.—H. Wrampelmeyer.—An apparatus for always adding 0·05 c.c. of mercury in determinations of nitrogen by Wilfarth's modification of the Kjeldahl process.

New Gas-generating Apparatus.—Max Kæhler (*Chemiker Zeitung*).—This apparatus, for its description, requires the accompanying figure. J. H. J. Dagger (Chemical News) has proposed a gas apparatus on the same principle. P. M. Chantemille (*Bulletin de la Soc. Chimique*) has also devised an analogous apparatus. J. Martin, P. Hart, and G. Stillingfleet Johnson have proposed and constructed very similar appliances (Chemical News).

Determination of the Specific Gravity of Solids.—H. Unger proposes an instrument very similar to that previously described by Gisevius (*Pharmacent. Zeitung*).

A Thermo-regulator for Temperatures between 40° and 60°.—E. Sehrwald (*Zeitschrift fur Wissensch. Microscopie*).—For the description we must refer to the original.

An Extraction Apparatus.—F. Schmidt and Haensch (*Chem. Centralblatt*).—The instrument agrees in principle with that proposed by C. M. King.

The Use of Hydrogen Peroxide for Analytical Purposes.—F. P. Dunnington (*Journal of Analytical Chemistry*).

An Evaporation-Stand.—A. Jolles (*Chemiker Zeitung*).—To which we refer for particulars.

A Washing-bottle for Ammonia.—F. M. Haldemann.—From the *Journal of Analytical Chemistry*.

Metallic Sponge as a Filtering Material.—O. E. Munroe (*Journal of Analytical Chemistry*).

Examination of Reagents as to Purity.—C. Krauch.—The author's instructions are not given.

Occurrence of Ferrous Oxide in Potassium Sulphocyanide.—J. Kranzfeld (*Pharm. Zeitung für Russland*).—Already inserted.

Preparation of Non-fermentible Starch-paste for Iodometric Purposes.—G. Gastine (*Bulletin Soc. Chimique*).

Determination of Ferric Oxide and Alumina in Presence of Lime and Phosphoric Acid.—G. Kennepohl (*Chemiker Zeitung*).—The hydrochloric solution, placed in a 100 or 200 c.c. flask, is neutralised with ammonia; to the neutral or slightly ammoniacal solution there is further added, disregarding any precipitation produced by the ammonia, a slight excess of oxalic acid, and the whole is heated for some time to 80°. After the calcium oxalate has fully settled the flask is cooled, filled up to the mark, filtered though a folded filter, and a measured quantity of the filtrate is evaporated to dryness in a platinum capsule. The dry residue is slightly ignited to destroy the oxalic acid, the residue moistened with strong ammonia, dried in the covered capsule, and finally dissolved in strong hydrochloric acid with the aid of heat. The solution is washed into a flask and the iron-alumina phosphate is precipitated with ammonia and acetic acid and further treated in the usual manner.

Use of Aniline as Absorbent for Cyanogen in Gas-Analysis.—Morris Loeb.—From the *Journal of the Chemical Society*.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Sugar Analysis.—Could any of your readers give me the name and price of a good book on the refining and analysis of sugars, and the analysis of bone chars?—Greenock.

To Wholesale and Retail Chemists.

IMPORTANT BUSINESS PREMISES, BURGES, COVENTRY.

MR. JAMES WHITTINDALE

Is instructed by the Trustee under the will of the late Mr. Thomas Bailey,

TO SELL BY AUCTION,

At his ESTATE ROOMS, Hertford Street, Coventry, on MONDAY, September 2nd, 1889, at Six o'clock in the Evening prompt, subject to conditions incorporating the Common Form Conditions of the Birmingham Law Society,

The very valuable and centrally-situated FREEHOLD PROPERTY, Nos. 4 and 5, Burges, Coventry, consisting of the excellent Retail Chemist's Shop with Dwelling House, comprising on the ground floor:—Entrance hall, sitting room, kitchen, and coal and boot-houses, w.c., &c., good cellar in the basement; on the first floor, large drawing room, chamber, and store closet; on the second floor, three chambers and box room; and on the upper floor are drug stores and attic.

At the rear of the Property known as No. 4 there are drug stores and offices on the ground and first floors, and on the second floor a large well-lighted warehouse.

The valuable business connection, together with the stock of the wholesale and retail trade and fixtures, may be taken, too, at a valuation or an agreed price, at the option of the purchaser.

The property is situated in one of the best thoroughfares in the city for business purposes, and was occupied by the late Mr. Thomas Bailey for over thirty years, where a most lucrative wholesale and retail druggist's business has been carried on.

Further particulars and permission to view may be had of Messrs. Woodcock and Co., Solicitors, or the Auctioneer, Coventry.

THE CHEMICAL NEWS.

Vol. LX. No. 1553.

ON THE CAVENDISH EXPERIMENT.*

By C. V. BOYS, A.R.S.M., F.R.S.,
Assistant Professor of Physics at the Normal School of Science, South Kensington.

The Cavendish experiment for determining the constant of gravitation, from which the density of the earth may be calculated, is so well known that there is no occasion to describe it. This experiment, devised by the Rev. John Mitchell, F.R.S., was first carried out by Cavendish,† and has been since performed by Reich,‡ Baily,§ and Cornu and Baille,‖ who have all followed very closely the arrangement of Cavendish.

Owing to the very small value of the constant of gravitation, all these experimentalists have aimed at increasing the sensibility as much as possible. With this object a long beam, carrying at its ends considerable masses, has been suspended by a very long and very fine wire. The attracting masses have been made as large as possible, and they have been brought almost into contact with the sides of the long box in which the beam is suspended. Cornu, it is true, has reduced the dimensions of all the parts to about one-quarter of the original amount. His beam, an aluminium tube, is only half a metre long, and it carries at its ends masses of ¼ lb. each, instead of about 2 lbs. as used by Cavendish. This reduction of the dimensions to about one-quarter of those used previously is considered by Cornu to be one of the advantages of his apparatus, because, as he says, if the period of oscillation is unchanged, then the sensibility is independent of the mass of the suspended balls, and is inversely as the linear dimensions. I do not quite follow this, because, as I shall show, if all the dimensions are increased or diminished together the sensibility will be unchanged. If only the length of the beam is altered and the positions of the large attracting masses, so that they remain opposite to and the same distance from the ends of the beam, then the sensibility is inversely as the length.

The other improvements introduced by Cornu are the use of mercury for the attracting masses, which can be drawn from one pair of vessels to the other without coming near the apparatus, the use of a metal case connected with the earth to prevent electrical disturbances, and the electrical registration of the movements of the index on the scale, which was placed 560 c.m. from the mirror. The period of oscillation which has been used has varied between 398 seconds (Cornu) and 840 seconds (Cavendish). Cavendish found that with the very inconvenient period of 1800 seconds the balls knocked against the side of the case.

The difficulty that has been met with has been the perpetual shifting of the position of rest, due partly to the imperfect elasticity or fatigue of the torsion wires, and partly, as Cavendish proved experimentally, to the enormous effects of air currents set up by temperature differences in the box, which with large apparatus it is impossible to prevent. In every case the power of observing was in excess of the constancy of the effect actually produced. The observations of Cornu are the only ones which are comparable in accuracy with other physical measurements, and these, as far as the few figures given enable one to judge, show a very remarkable agreement between values obtained for the same thing from time to time.

Soon after I had made and found the value of quartz fibres for producing a very small and constant torsion, I thought that it might be possible to apply them to the Cavendish apparatus with advantage. Professor Tyndall, in a letter to a neighbour written some months ago, expressed the conviction that it would be possible to make a much smaller apparatus, in which the torsion should be produced by a quartz fibre. Last summer I began to prepare an instrument with a working beam 5 m.m. long, but other experimental work obliged me to put this on one side for a time. I have lately examined the theory of this instrument in some detail, and as I find that in many particulars there is an advantage in departing from the arrangement that has always been employed, I have lately prepared two pieces of apparatus, which, on trial, fully bear out the results of this inquiry.

I shall, therefore, first give a short account of the principles that should be followed in the design of the Cavendish apparatus, and then describe the results which I have obtained up to the present time.

As I have already stated, the sensibility of the apparatus is, if the period of oscillation is always the same, independent of the linear dimensions of the apparatus. Thus, if there are two instruments in which all the dimensions of one are n times the corresponding dimensions of the other, then the moment of inertia of the beam and its appendages will be as $n^5 : 1$, and, therefore, the torsion also must be as $n^5 : 1$. The attracting masses, both fixed and movable, will be as $n^3 : 1$, and their distance apart as $n : 1$. Therefore, the attraction will be as n^3/n^2 or $n^1 : 1$, and this is acting on an arm n times as long in the large instrument as in the small; therefore the moment will be as $n^5 : 1$, that is, in the same proportion as the torsion, and so the angle of deflection is unchanged.

If, however, the length of the beam only is changed, and the attracting masses are moved until they are opposite to and a fixed distance from the ends of the beam, then the moment of inertia will be altered in the ratio of $n^2 : 1$, while the corresponding moment will only change in the ratio of $n : 1$, and thus there is an advantage in reducing the length of the beam until one of two things happens, either it is difficult to find a sufficiently fine torsion thread that will safely carry the beam and produce the required period, and this, I believe, has up to the present time prevented the use of a beam less than half a metre in length, or else, when the length becomes nearly equal to the diameter of the attracting balls, they then act with such an increasing effect on the opposite suspended balls, so as to tend to deflect the beam in the opposite direction, that the balance of effect begins to fall short of that which would be due to the reduced dimensions if the opposite ball did not interfere.

* * * *

If the position which is chosen for each attracting mass is nearer the plane of the beam than the transverse plane, that is, if the azimuth of the large masses is less than 45°, the best length of the beam will be more than half that which would bring the ends opposite the attracting masses.

It might be urged against this argument that a difficulty would arise in finding a torsion fibre that would give to a very short beam loaded with balls that it will safely carry a period as great as five or ten minutes, and until quartz fibres existed there would have been a difficulty in using a beam much less than a foot long, but it is now possible to hang a thing only half an inch long and weighing from 20 to 30 grains by a fibre not more than a foot in length, so as to have a period of five minutes. If the moment of inertia of the heaviest beam of a certain length that a fibre will safely carry is so small that the period is too rapid, then the defect can be remedied by reducing the weight, for then a finer fibre can be used, and since the torsion varies approximately as the square

* Extracts from a Paper read before the Royal Society, June 20, 1889.
† *Phil. Trans.*, 1798, p. 469.
‡ *Comptes Rendus*, 1837, p. 697.
§ *Phil. Mag.*, vol. xxi., 1842, p. 111.
‖ *Comptes Rendus*, vol. lxxvi., p. 954; vol. lxxxvi., pp. 571, 699, 1001.

of the strength (not exactly because fine fibres carry heavier weights in proportion), the torsion will be reduced in a higher ratio, and so by making the suspended parts light enough, any slowness that may be required may be provided.

Practically, it is not convenient to use fibres much less than 1-10,000th of an inch in diameter, and these have a torsion ten thousand times less than that of ordinary spun glass. A fibre 1-5000th of an inch in diameter will carry a little over 30 grains.

Since with such small apparatus as I am now using it is easy to provide attracting masses which are very large in proportion to the length of the beam, while with large apparatus comparatively small masses must be made use of owing to the impossibility of dealing with balls of lead of great size, it is clear that much greater deflections can be produced with small than with large apparatus. For instance, to get the same effect in the same time from an instrument with a 6 foot beam that I get from one in which the beam is 5-8ths of an inch long, and the attracting balls are 2 inches in diameter, it would be necessary to provide and deal with a pair of balls each 25 feet in diameter and weighing 730 tons instead of about 1¾ lb. apiece. There is the further advantage in small apparatus that if for any reason the greatest possible effect is desired, attracting balls of gold would not be entirely unattainable, while such small masses as two piles of sovereigns could be used where qualitative effects only were to be shown. Owing to its strongly magnetic qualities, platinum is unsuited for experiments of this kind.

By far the greatest advantage that is met with in small apparatus is the perfect uniformity of temperature which is easily obtained; whereas, with apparatus of large size, this alone makes really accurate work next to impossible. The construction to which this inquiry has led me, and which will be described later, is especially suitable for maintaining a uniform temperature in that part of the instrument in which the beam and mirror are suspended.

With such small beams as I am now using it is much more convenient to replace the long thin box generally employed to protect the beam from disturbance by a vertical tube of circular section, in which the beam with its mirror can revolve freely. This has the further advantage that if the beam is hung centrally the attraction of the tube produces no effect, and the troublesome and approximate calculations which have been necessary to find the effect of the box are no longer required. The attracting weights, which must be outside the tube, must be made to take alternately positions on the two sides of the beam, so as to deflect it first in one direction and then in the other. For this purpose they are most conveniently fastened to the inside of a larger metal tube, which can be made to revolve on an axis coincident with the axis of the smaller tube. There are obviously two planes, one containing and one at right angles to the beam, in which the centres of the attracting balls will lie when they produce no deflection. At some intermediate position the deflection will be a maximum. Now it is a matter of some importance to choose this maximum position for the attracting masses, because, in showing the experiment to an audience, the largest effect should be obtained that the instrument is capable of producing; while in exact measures of the constant of gravitatation this position has the further advantage that the only measurement which there is any difficulty in making, viz., the angle between the line joining the large masses and the line joining the small, which may be called the azimuth of the instrument, becomes of little consequence under these circumstances. In the ordinary arrangement the slightest uncertainty in this angle will produce a relatively large uncertainty in the result. I have already stated that if an angle of 45° is chosen the distance between the centres of the large balls should be $2\sqrt{2}$ times the length of the beam, and the converse of course is true. As it would not be possible at this distance to employ attracting balls with a diameter much more than 1¼ times the length of the beam, and as balls much larger than this are just as easily made and used, it will be well to find out what will be the position for maximum deflection when the centres of the attracting balls are any distance apart.

* * * *

If an attracting ball is placed in a position of maximum effect it will act on the further suspended ball, tending to deflect the beam in the opposite direction, and this will become more marked as the distance between the centres of the attracting balls increases, and so the increased effect which would be true to a greater attracting ball may be largely compensated by the increased action on the remote end of the beam. The azimuth at which the maximum effect is produced is also changed.

I have practically overcome this difficulty by arranging the two sides of the apparatus at different levels. Each large ball is at or near the same level as the neighbouring small ball, but one pair is removed from the level of the other by about the diameter of the large balls, which, in the apparatus which I have now the honour to submit to the Society, is nearly five times as great as the distance *in plan* between the two small balls.

In order to realise more fully the effect of a variety of arrangements I have, for my own satisfaction, calculated the values of the deflecting forces in an instrument in which the distance between the centres of the attracting balls is five times the length of the beam for every azimuth, and for differences of levels of 0, 1, 2, 3, 4, and 5 times the length of the beam.

(To be continued).

CONTRIBUTIONS TO THE CHEMISTRY OF STORAGE BATTERIES. No. 2.*

By E. FRANKLAND, D.C.L., F.R.S.

Under this title I communicated to the Royal Society, in February, 1883,† the results of some experiments on the reactions occurring during the charging and discharging of a storage cell. I showed that no appreciable part of the storage effect was due to occluded gases, as had been previously suggested by some chemists and physicists; but that the act of charging consisted essentially in the decomposition of lead sulphate, whilst the discharge was produced by the recomposition of this salt.

The establishment of these, as practically the only reactions going on in a storage cell, enabled me to prescribe a very simple method by which the charge in any cell could be ascertained, for as sulphuric acid is liberated during the charging and absorbed by the active material of the plates during discharge, the amount of charge could at any time be measured by ascertaining the amount of free sulphuric acid in the cell; in other words, by simply determining the specific gravity of the electrolyte; and this method has since been very generally adopted by the users of storage batteries.

In continuing these experiments it soon became evident that the lead sulphate formed and decomposed in the cell could not be the ordinary white sulphate hitherto known to chemists, because, in the first place, the active material of the plates always remains coloured even after discharge, and secondly, because whenever white sulphate is produced through abnormal reactions in the cell, it is afterwards decomposed only with extreme difficulty by the electric current.

In order to obtain some light upon the composition of the sulphate formed and decomposed in the cell, I have studied the action of dilute sulphuric acid upon litharge and minium.

* A Paper read before the Royal Society, June 20, 1889.

† *Proceedings of the Royal Society*, vol. xxxv., p. 67.

Action of Dilute Sulphuric Acid on Litharge.

Finely powdered litharge was treated with successive portions of dilute sulphuric acid until the liquid remains strongly acid after prolonged trituration. The resulting insoluble buff-coloured powder was washed with water till free from acid, and dried first at 100° C. and afterwards at 150—160°. The loss at this higher temperature was less than 0·2 per cent, and was therefore due to hygroscopic moisture.

PbO and SO_3 were then determined in the dried compound as follows :—The salt was dissolved in a small quantity of pure concentrated solution of caustic potash, and the solution, after dilution, was saturated with CO_2. (According to H. Rose, COPbo″ is soluble in $COKo_2$, but not in COHoKo). Any excess of CO_2, which might have caused the COPbo″ to dissolve, was avoided by warming the liquid with the precipitate on the water-bath to a temperature at which the COHoKo begins to dissociate. The liquid was then allowed to cool and stand twelve hours before filtering. The COPbo″ was filtered off, converted into nitrate, and precipitated and weighed as sulphate. The sulphuric acid was determined in the filtrate from the COPbo″.

1·2964 grms. of the salt gave 0·6647 grm. baric sulphate and 1·4437 grms. plumbic sulphate.

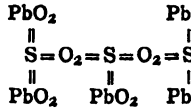
These numbers agree closely with the formula—

$$(SO_3)_3(PbO)_5,$$

as is seen from the following comparison of calculated and experimental numbers :—

	Calculated.		Found.
$3SO_3$	240	17·71	17·61
$5PbO$	1115	82·29	81·96
	1355	100·00	99·57

These analytical results suggest the following graphic formula :—



The formation of this salt may be represented by the following equation :—

$$5PbO + 3SO_4H_2 = S_3Pb_5O_{14} + 3OH_2.$$

Litharge. Sulphuric acid. Buff lead salt. Water.

Action of Dilute Sulphuric Acid on Minium.

Minium was treated with dilute sulphuric acid in exactly the same way as litharge, and the resulting brownish red compound dried first at 100° C. and afterwards at 150—160°. The loss at this higher temperature was again less than 0·2 per cent.

PbO, SO_3, and excess of oxygen were then determined in this salt in the following manner :—The salt was first treated with concentrated hydrochloric acid in order to reduce all the lead to the mon-oxide stage. The resulting mixture was then dissolved in caustic potash and treated as already described. The excess of oxygen was determined by finding the loss of weight which resulted from the evolution of CO_2 when the salt was treated with oxalic acid and dilute nitric acid.

2·1136 grms. of the salt gave 1·1978 grms. baric sulphate and 2·2710 grms. lead sulphate.

1·5110 grms. treated with oxalic acid and dilute nitric acid evolved 0·0910 grm. CO_2.

These numbers correspond to the following percentages :—

SO_3	19·45
PbO	79·03
O	1·09
	99·57

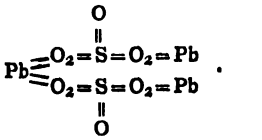
which agree with the formula—

$$S_2Pb_3O_{10},$$

as is seen from the following comparison :—

	Calculated.		Found.
S_2	64	7·57	7·78
Pb_3	621	73·49	73·36
O_{10}	160	18·94	18·43
	845	100·00	99·57

The composition of this salt may be represented graphically, thus—



The formation of this salt is expressed by the following equation :—

$$Pb_3O_4 + 2SO_4H_2 = S_2Pb_3O_{10} + 2OH_2.$$

Minium. Sulphuric acid. Red lead salt. Water.

These, then, are the salts which constitute the original active material of storage cells when that material is formed by the admixture of sulphuric acid with litharge or minium respectively, and it is highly probable that one or the other of these salts takes part in the electrolytic processes of the storage battery. It is fortunate that these hitherto unknown salts (and not the ordinary known sulphate) are formed in the cell reactions; for, in the alternative case, lead storage batteries would be practically valueless.

If the buff lead salt be the active material of the battery plates, then the following equations express the electrolytic reactions taking place in the cell :—

I. In charging—

(*a*). *Positive Plates.*

$$S_3Pb_5O_{14} + 3OH_2 + O_5 = 5PbO_2 + 3SO_4H_2.$$

Buff lead salt. Water. Lead peroxide.* Sulphuric acid.

(*b*). *Negative Plates.*

$$S_3Pb_5O_{14} + 5H_2 = 5Pb + 3SO_4H_2 + 2OH_2.$$

II. In discharging—

(*a*). *Positive Plates.*

$$5PbO_2 + 3SO_4H_2 + 5H_2 = S_3Pb_5O_{14} + 8OH_2.$$

(*b*). *Negative Plates.*

$$5Pb + 3SO_4H_2 + O_5 = S_3Pb_5O_{14} + 3OH_2.$$

If the red lead salt be the active material, then the following equations express the same electrolytic reactions :—

I. In charging—

(*a*). *Positive Plates.*

$$S_2Pb_3O_{10} + O_2 + 2OH_2 = 3PbO_2 + 2SO_4H_2.$$

Red lead salt. Lead peroxide. Sulphuric acid.

(*b*). *Negative Plates.*

$$S_2Pb_3O_{10} + 4H_2O = 3Pb + 2SO_4H_2 + 2OH_2.$$

II. In discharging—

(*a*). *Positive Plates.*

$$3PbO_2 + 2SO_4H_2 + 2H_2 = S_2Pb_3O_{10} + 4OH_2.$$

(*b*). *Negative Plates.*

$$3Pb + 2SO_4H_2 + 2O_2 = S_2Pb_3O_{10} + 2OH_2.$$

An inspection of these equations discloses, in the case of the red lead salt, a fact which has already been roughly

* Mr. Fitzgerald considers that this peroxide is hydrated.

observed in practice, viz., that only half as much active material is electrolytically decomposed on the negative as on the positive plates; whence it follows that the weight of active material on the negative plates need not exceed one-half of that upon the positive plates; for, in the decomposition of the electrolyte, equivalent quantities of oxygen and hydrogen are evolved; that is to say, two atoms of hydrogen for each atom of oxygen. But in the decomposition of the red lead salt four times as many atoms of hydrogen are required to reduce the salt to metallic lead as atoms of oxygen which are necessary to transform the lead of the salt into peroxide. When, however, the active material of the positive plate has once been converted into peroxide of lead, it seems probable that the red salt only is formed; at all events, until the discharge at high potential is nearly completed, when there are indications of the production of the buff-coloured salt. But this is a point requiring further investigation.

I have to thank Dr. F. R. Japp, F.R.S., for his assistance in the analytical work of this investigation.

RAPID FILTRATION.

By REGINALD A. FESSENDEN,
Chemist, Edison Laboratory, Orange, N.J.

THE use of filter-pumps, as every chemist is aware, does not, in a very great number of cases, facilitate filtration: 1st, because a dense layer of the precipitate forms next the paper, which continually requires to be removed, and 2nd, if any considerable pressure is used particles of the precipitate will pass through.

FIG. 1.

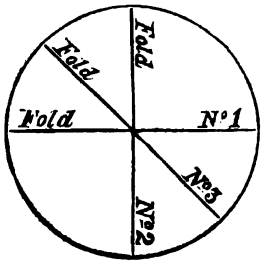
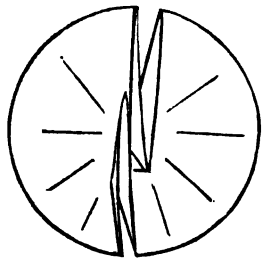


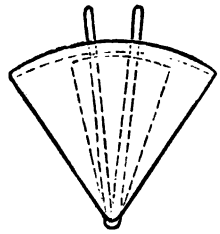
FIG. 2.



To increase the surface seems to be the better plan. Plaited filters partially effect this, but the precipitate cannot be easily detached from them, and they are troublesome to prepare. Ribbed funnels, while also an improvement, have only one side of the filter for use, the other side being covered with three thicknesses of filter-paper.

FIG. 3.

FIG. 4.

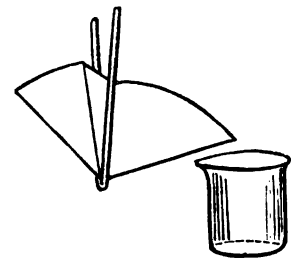


The following method enables filtrations to be made very rapidly, and in such a manner that the precipitate can be readily removed:—

The filter-paper is folded three times; folds Nos. 1 and 2 are towards the reader, No. 3 from him. The filter is then gathered (Fig. 2), and a piece of glass rod, bent at a very acute angle, inserted in the cleft of the filter (Figs. 3 and 4), thus giving a filtration surface of nearly four times the usual one.

The filtration being complete, the glass rod is grasped by the projecting ends and lifted from the funnel, bearing the filter upon it. One end of the filter-paper is then

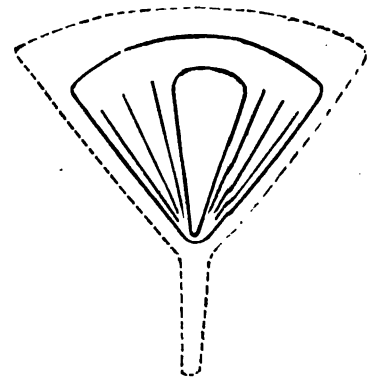
FIG. 5.



bent down, and the precipitate is easily washed off (Fig. 5).

An improvement on this is to use, instead of the glass rod, a plate of glass (Fig. 6) ribbed on both sides. This

FIG. 6.



renders the filtration very rapid indeed, and if it were made by the manufacturers of chemical apparatus, would no doubt be used.

From the Laboratory of
Thomas A. Edison.

ELECTROLYTIC SEPARATIONS.*

By EDGAR F. SMITH and LEE K. FRANKEL.

1. *Separation of Cadmium from Copper.*

THE results obtained in the electrolysis of cyanide solutions of mercury and copper, as well as the knowledge gained from our experiments in separating cadmium from zinc, induced us to try whether it would be possible to effect the separation of cadmium from copper in cyanide solution. The only electrolytic method proposed for the separation of these metals is that recommended by Smith (*Am. Chem. Journ.*, ii., 42), in which solutions containing a definite amount of free nitric acid were employed. We experienced no difficulty in making a complete separation after ascertaining the proper current strength. The conditions most favourable to the separation were essentially the same as those recorded in our former papers, viz., a dilution of 200 c.c., 5·5 grms. of potassium cyanide in each experiment, and a current generating 0·28 c.c. oxy-

* Read at the Meeting of the Chemical Section of the Franklin Institute, June 18, 1889.

hydrogen gas per minute. Time, sixteen to twenty hours. The results obtained were as follows:—

I.

Cadmium present.	Cu present.	Cadmium ound.
0·2426 grm.	50 per cent	0·2420

II.

Cadmium present.	Cu present.	Cadmium found.
0·2318 grm.	50 per cent	0·2331
	,,	0·2309
	,,	0·2315

III.

Cadmium present.	Cu present.	Cadmium found.
0·1024 grm.	100 per cent	0·1028
	,,	0·1019
	,,	0·1020
	,,	0·1032
	,,	0·1033
	,,	0·1034
	,,	0·1014

IV.

Cadmium present.	Cu present.	Cadmium found.
0·2046 grm.	100 per cent	0·2034

Copper was not found in any of the deposited cadmium, nor did we discover any of the latter metal in the filtrate containing the copper. The cadmium deposit invariably showed the grey colour characteristic of it.

II. *Action of the Current upon Metallic Sulphocyanides.*

It is well known that in the electrolysis of the sulphate or nitrate of manganese the oxide of this metal separates upon the positive pole. We have found that if an excess of potassium sulphocyanide be present no such deposition occurs, but, on the contrary, the metal itself will separate as a greyish white compact deposit upon the negative pole or the vessel attached to it. The addition of a sulphocyanide to the manganese solution undergoing electrolysis, after the oxide has already separated, will cause the solution of the latter. The current necessary for the deposition of metallic manganese, under the conditions mentioned above, should be feeble. The metallic deposit is inclined to rapidly oxidise, and whether manganese can be successfully determined in a quantitative way after this manner will depend very much upon whether we can prevent its oxidation during the drying process.

Nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current.

Chemical Laboratory, Univ. of Pa.,
Philadelphia, June 18, 1889.

ON THE

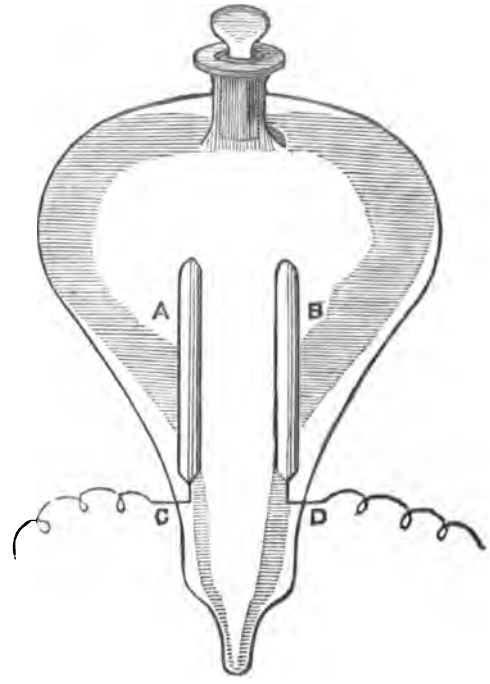
BLEACHING EFFECTS OBSERVED DURING THE ELECTROLYSIS OF ACIDIFIED WATER.

By H. N. WARREN, Research Analyst.

While recently demonstrating upon the electrolysis of water, I caused the acidulated water contained in the voltameter which was employed for that purpose to be coloured blue by the addition of a small quantity of sulphate of indigo, so that the passage into, and, at the same time, the collection of the gases in their respective tubes, might be the more readily observed.

On decomposition of the water being accomplished by the aid of four Bunsen cells, it was observed, after the lapse of a few minutes, to have assumed an entirely greenish tint, which almost directly afterwards completely disappeared, leaving the water perfectly colourless.

After the performance of several experiments, with a view of ascertaining the effects on a more efficient scale, the following apparatus was devised:—As shown in the diagram, it consists essentially of an ordinary separating funnel, into the sides of which are secured, by fusing, two thick platinum wires, namely, C and D; these are connected with two graphite pencils, A and B, the surface of each being prepared by introducing the same into a concentrated solution of platinum nitrate, and afterwards heating to redness, out of contact with air. On connecting the extremities of the platinum wires with a battery consisting of four Bunsen cells, and having, previous to this, introduced into the globe about half a litre



of an acidified and concentrated solution of sulphate of indigo, after the lapse of a quarter of an hour the blue colour, which, at the commencement of the action, was of the usual deep tint natural to indigo, had become transformed into a perfect green, which, as in the former experiments, speedily became colourless. Turmeric, tincture of yellow berries, logwood, cochineal extracts were also as successfully bleached. In a further experiment a piece of indigo dyed cloth was suspended between the carbon poles, and at the termination of two hours was almost destitute of any blue colouration. Several samples of raw yellow cotton were also successfully bleached when exposed to the same action; while nitrogenous products such as wool, and also solutions of the various unrefined sugars, experienced little, if any, change.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

Alcohol in Ethereal Oils.—H. Hager (*Ph. Zeitung*) determines such alcohol approximately by pouring the sample into a narrow test-tube and shaking it well up with pure glycerin. The glycerin rapidly and completely withdraws from the oil any alcohol which is present, and its quantity may be approximately estimated by the increase of the volume of the glycerin. In oils containing acids or similar constituents this method does not give accurate results.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, August 10th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

One sample, out of the 189 examined, manifested a "very slight turbidity." The remaining 188 samples were found to be clear, bright, and well filtered.

Despite the unfavourable influence of the stormy weather prevailing more or less throughout the month, the condition of the water supply, furnished by each of the seven Companies respectively, was found to be entirely satisfactory. In our report for the previous month of June, we had to record a slight increase in the mean proportion of organic carbon present in the supply, as compared with that present in the supply for the preceding month of May. This slight increase, due, it would seem, to the casual occurrence of a flooded state of the rivers, was not found to be sustained in the supply for the past month of July. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in 100,000 parts of the water during each of the last three months respectively, was found to be as follows:—

Parts of Organic Carbon in 100,000 *Parts of Water.*

May	0·144
June	0·157
July	0·137

The mean proportion of organic carbon present in the July supply constitutes, accordingly, the lowest monthly mean yet met with during the year; while the maximum proportion met with in any single July sample, or 0·153 part in 100,000 parts of the water, falls a little short of the mean proportion for the preceding month of June—this last proportion, moreover, constituting also the mean proportion for the first six months of the year. The above detailed result of the determination of organic carbon is fully corroborated by the results of the determination of the amounts of oxygen required for the oxidation of the organic matter present in the water, and of the determination of the degree of freedom of the water from colour-tint.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE COLOURED REACTION OF CARBON COMPOUNDS.*

By EMIL NICKEL.

THE author points out that the colour-phenomena adduced as the reactions of single bodies are for the most part not confined to the substances in which they were first observed, but such colour-reactions are almost always common to a whole group of bodies if brought in contact with the reagent in question. For the identification of such substances it is therefore necessary to submit them to the action of a number of reagents.

Every kind of coloured reaction seems to point to the presence of a definite group of atoms, and by the combination of several such reactions it is possible not merely to recognise such a body with certainty, but by systematically following out this point of view we may obtain a more or less complete insight into the constitution of the compound in question.

1. *Colour Reactions under the Influence of Nitrous Acid, Exclusive of the Formation of Azo-colours.*

a. Reactions with Millon's Reagent.—For the preparation of the reagent the author finds it most convenient to dissolve 1 c.c. of mercury in 9 c.c. nitric acid of sp. gr. 1·52 and to dilute with an equal volume of water. The effective constituents of the reagent are the mercuric and mercurous nitrates and free nitrous acid. The solution becomes useless on prolonged keeping, but it can be restored by the addition of potassium nitrite. As a rule, 1 or 2 drops of Millon's reagent are to be applied to 1 to 2 c.c. of the solution in question; the colouration comes up best at 60°, 70°, or 100°; in some instances, *e.g.*, thymol, the colour first produced is destroyed by boiling.

As to the substances which yield a colour with Millon's reagent, the author finds that it is always aromatic compounds in which one hydroxyl-group (OH) or the derived methoxyl-group ($O-CH_3$) is fixed on a benzol or naphthaline nucleus.

The reaction occurs also when along with the hydroxyl-group an aldehyd or carboxyl-group or a lateral chain is joined to the benzol nucleus, or even when hydroxyl or amido-groups occur in the lateral chain. But if a nitro-group or a second hydroxyl-group is attached to the benzol nucleus no red colour is produced by Millon's reagent. Thus, resorcine gives a yellow colour, pyrogallol a brown, and hydroquinone an orange. On the other hand, tannin, which contains several hydroxyls bound to the benzol nucleus, gives, with Millon's reagent, a red colour, which soon disappears and is not permanent in heat.

Whilst, therefore, it is not to be expected that compounds which contain simultaneously a hydroxyl-group and a methoxyl-group on the benzol nucleus will give no reaction, there results with guiacol (certainly not chemically pure) a red colour, and with eugenol and vanilline a very decided violet.

Hofmann's Reagent consists of a solution of mercuric nitrate with a trace of free nitrous acid, whilst

c. Plugge's Reagent consists of a solution of mercurous nitrate with a little free nitric acid.

The manner of application and the sphere of action are in both cases analogous to those of Millon's reagent, but in many cases there appear small differences which point to a different behaviour of the two stages of oxidation of the mercury.

d. Liebermann's Colour Reactions.—If 100 parts of sulphuric acid and 5 parts of potassium nitrite are let act upon phenols we obtain, as Liebermann has shown, colourations of different kinds. If the question is not the application of this reaction to the production of colouring-

* An Inaugural Dissertation presented to the Philosophical Faculty of the University of Jena.

matters, but to recognise one or other substance, such substances must be allowed to react in dilute solutions, whilst Liebermann prefers the use of the phenols undissolved, or at least in a concentrated solution.

The author finds that the monophenols are distinguished by the production of intense colours, whilst, among the polyvalent phenols, only orcine yielded a strong red colouration, and the remaining for the most part gave merely a faint yellowness.

Liebermann's reaction resolves itself into two phases. The phenols unite with nitrous acid to nitrosophenols, and the latter, under the condensing influence of the sulphuric acid, form the colouring-matter with the unchanged part of the phenol.

The reaction can therefore be effected by letting phenols, nitrosophenols, and sulphuric acid act upon each other. In this form the reaction is applicable to the nitrosophenols.

e. New Colour-Reactions with New Reagents.—In connection with Liebermann's reaction the author has endeavoured to use, instead of sulphuric acid, other condensing agents, in case of need, with the aid of heat. In this manner he has been led to use various metallic salts of the mineral acids, along with an alkaline nitrite and free acid, although the latter was in many cases not advantageous. These reagents act primarily upon the phenols or the oxy-aromatic compounds. The author makes two reactions especially prominent, though without regarding them as decisive for the organic compounds concerned.

If a solution of vanilline is boiled with a solution of mercuric chloride containing potassium nitrite, there appears, in a few minutes, a fine violet colour. The sensitiveness depends somewhat upon the composition of the reagent, but it is certainly equal to that of the reaction with a solution of an aniline salt.

If we add to a solution of phlorhizine an excess of solid potassium nitrite, then a little solid zinc sulphate, and boil the solution, there appears a blue or violet colour. Some other glycosides which the author examined (coniferine, salicine, quercitrine) displayed, when similarly treated, no colouration.

2. Coloured Reactions with Formation of Azo-colours.

a. Weselsky's Reaction and its Extensions.—Weselsky originally recommended the use of potassium nitrite and aniline nitrate for the detection of phloroglucine. Of course another salt of aniline, *e.g.*, the sulphate, can be used as well. The author obtained very fine coloured reactions with salts of toluidine, xylidine, and naphthylamine.

Instead of producing diazo-compounds by mixing the above-named amidic bodies with a nitrite upon the action of which the production of the colour depends, the diazo-compounds may be used directly.

Among bodies not technically important or not exclusively so, Weselsky has observed that phloroglucine, and also catechine and maclurine, yield, with his reagent, red colours. Procter (Chemical News) has sought to ascertain if all the phloroglucides (*i.e.*, the numerous vegetable principles which, on their decomposition, yield phloroglucine) produce this reaction, but without having come to a definite solution of the question.

In his experiments with the phenols carried out as above the author obtained almost exclusively brown or yellow colours. With resorcine he obtained red colours, which differed slightly according to the diazo-compound employed. With phorhizine and with several aldehyds he obtained red colours.

b. Colour-Reactions with Para-diazo-benzol-sulphuric Acid (Ehrlach's Reaction).—The accounts of these colour-reactions relate almost exclusively to the researches of Ehrlich, Petri, Penzoldt, and Fischer and Penzoldt, already given in the *Zeitschrift für Analytische Chemie.*

3. Colour-Reactions with Formation of Triphenylmethane Colours and Analogous Compounds.

a. Colour-Reactions of the Phenols with Aldehyds.—The author has chiefly studied the behaviour of phenol, pyrocatechine, resorcine, hydroquinone, pyrogallol, and phloroglucine with aldehyds and some other compounds, and points out that the solutions requisite for such reactions should not be kept, as they readily suffer decomposition. By the direct action of the phenols upon the aldehyds under suitable conditions we scarcely obtain a colouration. This appears only on the simultaneous presence of an acid. The author mentions, as a theoretical basis of this fact, the circumstance that the triphenylmethane colouring-matters in question are distinguished from such compounds as rosaniline, aurine, and phthalein, thereby, that in the former the fourth hydrogen atom of the methane is present unchanged, whilst in the latter compounds it is eliminated or substituted.

The author's attempts to obtain colour-reactions in very dilute cold solutions led to no satisfactory results.

On adding a sufficient quantity of acid and applying heat in case of need the phenols were found to be very useful reagents for aldehyds, though the colour-reactions were not confined to the latter. The author has obtained very fine reactions with nitrogenous bodies, alloxan and creatinin, on boiling with phenols and acids.

b. The Phenols as Reagents for Lignine.—In connection with the above the author shows that probably all the phenols give well-marked colour-reactions with wood in presence of an acid. Nickel considers phloroglucine as the best reagent for wood. An intense violet-red colouration is produced by lignine in contact with phloroglucine and an acid.

c. The Aldehyds as Reagents for the Phenols.—This is merely an inversion of the reactions given under *a*. For the detection of phloroglucine Nickel recommends wood or wood-stuff paper in presence of hydrochloric acid.

d. Salts of Aniline, Toluidine, &c., as Reagents for Aldehyds.—The above substances, either in alcoholic or or aqueous solution or in the solid state, and in general without the presence of acids, yield coloured reactions with a series of substances. As an example, Nickel mentions the yellow colour (first observed by Singer) produced on the contact of a solution of an aniline salt with solutions of the vanilline salts. The reaction is not specific, since it occurs with salicyl-aldehyd. It does not, however, extend to all the aromatic aldehyds, as cinnamol gives no colouration with aniline sulphate.

He discusses the furfurol reactions with aniline sulphate and with xylidine acetate observed by Stenhouse, Jorissen, Förster, and Schiff, and regards the reaction as probably not limited to furfurol.

Benzophenone, acetophenone, and acetacetic ether give no colour with aniline sulphate, though eugenol, which belongs to the phenols, gives a yellow colour.

Among the glycosides, coniferine alone gives a yellow colour with solution of aniline salt, which is faint in solutions, distinct with the solid, and very intense on the addition of acids.

Salts of aniline and toluidine are reagents for lignine.

The presence of potassium bisulphite, which unites with the aldehyds and analogous compounds, prevents the reactions above-mentioned.

The author notices the reactions mentioned by Lustgarten, and shows that they probably belong to the group of reactions just mentioned.

4. Colour-Reactions with Ferric Salts and with Chromates.

Ferric chloride, which gives coloured reactions with a great number of organic bodies is best applied in a dilute watery solution.

Among the organic bodies, which give colours with ferric chloride three groups are mentioned.

1. The oxy-aromatic bodies which have an hydroxyl-group at the nucleus.

2. Aromatic bodies containing an amidic group at the nucleus.

3. The carbon acids.

5. Colour-Reactions with Chromates.

Setting out from Sanio's proposal to use potassium dichromate for the microchemical detection of the tannic acids, which produces with them a dark red or brown precipitate, Nickel mentions some special cases of tannin reactions, and describes his experiments on the extension of the sphere of these reactions. Some phenols and aromatic azo-compounds have a remarkable behaviour.

Pyrocatechine, according to its concentration, gives, with the alkaline dichromates, a brown or black colour or a dark precipitate. Hydroquinone behaves in the same manner, whilst resorcine gives no colour.

Pyrogallol gives a brown precipitate, and a hot solution of α-naphthol a brown colour. With guaiacol, orcine, and phloroglucine Nickel obtained no reaction. Among the carbon acids gallic acid gives a decided precipitate, whilst pyrocatechuic acid reacts only in strong solutions and forms no precipitate.

As regards the amines, Nickel mentions the brown colour produced by solution of dichromate with aniline and xylidine.

In conclusion the author mentions the colour-reactions produced by the oxidising agency of the dichromate in presence of an acid, and refers here to the behaviour of the alkaloids.—*Zeitschrift für Analytische Chemie*, vol. xxviii., p. 244.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

(Concluded from p. 93).

Watch Jewels.—About 1,200,000 watches with jewelled works are annually manufactured in the United States, requiring about 12,000,000 jewels, 7 to 21 for each watch; of these 5,000,000 are ruby and sapphire and 7,000,000 are garnet jewels, valued at over 300,000 dollars. Most of them are imported, but the Waltham Company does its own cutting, employing in this department about 200 hands under the superintendence of Mr. W. R. Wills. About 15,000 carats of bort, in powdered form, are used annually in slitting and drilling these jewels. Nearly all the ruby, sapphire, and garnet used for jewels are imported, but it is hoped that American materials will soon be used. To be of value for this purpose, the material must be of some decided shade of red or blue, of a hardness greater than quartz, and free from flaws.

During the last decade new stones have come into favour, some neglected ones have regained their popularity, and still others, such as the amethyst and cameos, have been thrown out entirely. The latter, no matter how finely cut, would not find purchasers now at one-fifth of their former value; about ten years ago they were eagerly sought after at from four to twenty times the present prices. Rubies were considered high ten years ago, and a further rise was not looked for, but to-day they are still higher, a $9\frac{A}{8}$ carat stone having been quoted at 33,000 dollars. There is no demand at present for topaz, yet a syndicate of French capitalists has been organised to control the topaz mines of Spain, in the expectation that after twenty years of disfavour this gem will again be popular. Coral has felt the change of fashion, for during the last three years the imports have been less than 1000 dollars per annum, and in the last ten years in all 33,956 dollars, whereas in the ten years preceding 388,570 dollars worth were imported. The popularity of amber, on the other hand, is increasing. The imports of amber beads for the ten years 1868 to 1878, amounted to less than 5000 dollars, whereas, during the last ten years 35,897 dollars worth have been introduced. Amber amounting to only 47,000 dollars was imported from 1868 to 1878, but over 350,000 dollars worth from 1878 to 1888. Brazilian pebbles worth 65,000 dollars have been cut or sold ready for re-grinding since 1878, and less than 3000 dollars in the ten years preceding.

Ten years ago few of our jewellers carried more than the following stones in stock:—Diamond, ruby, sapphire, emerald, garnet, and occasionally a topaz or aquamarine. The gem and mineralogical collections contained a large series of beautiful stones, hard, and of rich colour, but known here as "fancy stones," and by the French as *pierres de fantasie*. Since then considerable interest has centered in these fancy stones, and any leading jeweller is not only expected to be familiar with, but to keep almost all of them in stock. This change may be partly referred to the fact that since the Centennial Exhibition art matters have received more attention among us than before.

The Duke of Connaught gave his bride elect a cat's-eye ring as an engagement token; this was enough to make that stone fashionable and to increase its value greatly. The demand soon extended to Ceylon, where the true chrysoberyl cat's-eye is found, and stimulated the search for them there. In the chrysoberyl cat's-eye the effect is the result of a twinning of the crystal, or of a deposit between its crystalline layers of other minerals in microscopic inclusions. If the stone be cut across these layers *en cabochon*, or carbuncle cut, as it is called, a bright line of light will be noticed on the dome-like top of the stone. In price they range from 20 dollars upwards; exceptional stones have sold at from 1000 to 8000 dollars.

In the search for these chrysoberyl cat's-eyes an endless series of chrysoberyls has been found, of deep golden, light yellow, yellow green, dark green, sage-green, yellowish brown, and other tints. They are superb gems, weighing from 1 to 100 carats each, ranking next to the sapphire in hardness. They gave a great surprise to the gem dealers; for it was found that the darker leaf-green or olive-green stones possessed the wonderful dichroitic property of changing to columbine red by artificial light, the green being entirely subdued and the red predominating. They were, in fact, alexandrites, a gem which had formerly been found only in Siberia, and even there of poor quality; though found in large crystals, a perfect gem of even 1 carat was a great rarity. Here, however, fine gems but rarely under 4 carats were found, and an exceptional one weighed 67 carats. They can be numbered among the most remarkable gems known. Strange to say, among this alexandrite variety a few have been found which combine the characteristics of the cat's-eye and the alexandrite, and were accordingly named the alexandrite cat's-eye.

Moonstones also from this same province of Kandy, Ceylon, were brought to light by this search for cat's-eyes. It would not be an over-estimate to say that 100,000 of these stones have been mounted here in the last four years. They vary in size from one-eighth of an inch to nearly 2 inches long and 1 inch thick, and many of them surpass anything hitherto known of their kind in beauty and size, selling from 50 cents to 100 dollars each, in a few exceptional cases 150 dollars. Those displaying the *chatoyant* white and the opalescent blue colour are especially beautiful.

The demand for the cat's-eye also brought into demand the then rare mineral from the Orange river, South Africa, known as crocidolite, more especially that variety that has been altered to a quartz cat's-eye. In this stone an infiltration of siliceous material coated each fibre with quartz or chalcedony, giving it the hardness of 7. This pleasing stone readily sold for 6 dollars a carat, and at the outset for even more; but owing to the excessive competition of two rival dealers, who sent whole cargoes of it to the London market, the price fell to 1 dollar, or even to 25 cents per pound in large quantity. Even table tops have been made of this material by veneering.

* Abstract from "Mineral Resources of the United States."

Vases, cane heads, paper weights, seals, charms, &c., were made of it, and sold in large quantities. Burning it produced a bronze-like lustre, and by dissolving out the brown oxide of iron colouring an almost white substance was obtained, which was dyed by allowing it to absorb red, green, and brown coloured solutions. These, owing to the delicacy of the fibres, were evenly absorbed. Ten years ago this material was practically unknown, but so extensively has it been sold that to-day it is to be found at every tourist's stand, whether on the Rigi, on Pike's Peak, in Florida, at Los Angeles, or at Nishni Novgorod, showing how thoroughly organised is the system of distribution in the gem market. The green quartz cat's-eye from Hof, Bavaria, has also been brought into use and quite extensively sold, but at present both these varieties are only used in the very cheapest jewellery.

Since it has become generally known that Queen Victoria is partial to the opal, the old and stubborn superstition concerning it, which is said to date from Scott's "Anne of Geierstein," has been slowly yielding, until now the gem has its share of public favour. During the last two years ten times as many opals have been imported as were brought here during the preceding decade, many of these being the fine Hungarian stones. Mexican fire opals are much more common, as those tourists know to their sorrow who buy these stones at exorbitant prices in Mexico, hoping thus to pay the expenses of their trip, until they find on reaching New York that they are worth only about a quarter of what they paid for them.

The opal mines of Mexico are situated on the Hacienda Esperenza, near Queretaro. It is believed that a demand of 50,000 stones per annum could be supplied without raising the price perceptibly.

The opal mines of Dubreck, Hungary, yield the Government a revenue of 6000 dollars annually. The output is so carefully regulated that the market is never glutted.

About ten years ago a new and very interesting variety of opal was brought from the Baricoo river, Queensland, Australia, where it was found in a highly ferruginous jasper-like matrix, sometimes apparently as a nodule and then again in brilliant coloured patches, or in specks affording a sharp contrast with the reddish brown matrix, which admits of a high polish and breaks with a conchoidal fracture. Many of these stones are exceedingly brilliant. They are of the variety known as harlequin opals, their colour being somewhat yellow as compared with the Hungarian stone, although not less brilliant. The rich ultramarine blue opal is quite peculiar to this locality, and the green variety almost transcends the Hungarian, A company capitalised at £200,000 has been formed, and the gems are extensively mined. Many curious little cameo-like objects, such as faces, dog's heads, and the like, are made by cutting the matrix and the opal together.

Green beryls, blue and green sapphires, white and bluish topaz, garnets, and zircons have been found at New England, in New South Wales, and precious opals are obtained from the Abercrombie river.

During the last ten years the taste for collecting jade and other carved hard stone objects has greatly increased, especially among Americans, owing to the stimulus given by the Centennial, Paris, and Amsterdam expositions, and the breaking up by sale of many of the large collections. The value of carved jades outside of China and India cannot be far from 2,000,000 dollars.

In the United states there are, perhaps, twenty buyers, who have purchased fully 500,000 dollars worth of this material, many of the pieces being among the finest known, such as the private seal and other objects from the sacking of the Emperor of China's summer palace. The finest pieces, brought over by Tienpau, included some of the best that ever left China, and were intended for the Amsterdam exhibition; the choicest specimens of the Wells, Guthrie, Michael, and Hamilton Palace collections are now owned in the United States. Experienced agents have been frequently sent to India and China to secure the finest objects as they presented themselves. One collection alone is worth over 100,000 dollars; single objects sometimes selling for over 5000 dollars, and one exceptionally fine specimen being valued at over 10,000 dollars. Explorations in Alaska have brought to light the fact that jade was used by the natives for implements, and it is almost proved that it is found not only as boulders but also *in situ*. The National Museum, the Emmons, Everett, Peabody Museum, Canadian Geological Survey, Dresden, and other collections, including the writer's own, contain several hundred objects, at least, that are made of this Alaskan material. A fact of interest in this connection is that Prof. F. W. Clarke found among the objects collected for the National Museum one which, on analysis, proved to resemble pectolite so closely that he referred it to that species. It has the hardness of jade, a specific gravity of 2·873, and is pale green in colour. The same discovery was made almost simultaneously by foreign observers.

The theory that jadeite or chalchiuitl was highly prized by the aborigines has been greatly strengthened during the last ten years. Prof. J. J. Valentine, in his paper before the American Antiquarian Society, April 27, 1881, on the Humboldt celt or votive adze and the Leyden plate, two remarkable carved jadeites, offered some exceedingly interesting suggestions. The Humboldt celt was presented to Humboldt by Del Rio in 1803, and the Leyden plate was given to that museum by A. S. Von Bramm, who found it near St. Felipe, close to the borders of Guatemala, in Honduras. They are both 9 inches in length and 3¼ inches wide; the former 1⅜ inches in thickness, and the latter only ½ inch. This similarity of dimensions suggests to me that the two objects were originally part of one and the same celt. Before the same Society, in April, 1886, Professor Putnam exhibited his remarkable series of Nicaragua and Costa Rica jadeites, which were all ornaments made by cutting into halves, thirds, or quarters one large celt perforated by one or two drilled holes, in one instance two of them fitting together. The 16-pound adze exhibited by myself at the American Association for the Advancement of Science meeting of 1887, from which fully two pounds had been cut; the breastplate recently found measuring only one-half inch thickness; and the fact that even Burmese jadeite, when burned or exposed to a high temperature, will assume the greyish green colour of the Mexican, all tend to support Professor Fisher's theory that this jadeite originally came from there. Additional evidence is the striking resemblance between the Maya and ancient Burmese styles of carving, although Dr. Meyer, of Dresden, firmly believes that this material will yet be found *in situ* in Mexico. The imperial jade quarries of Burmah, in the Mogung district, 90 miles from Bhamo, are leased by two companies, who pay a royalty of 30,000 dollars annually. The trade is entirely in the hands of the Chinese. At the Colonial Exhibition in London in 1886 there were exhibited large rounded and waterworn blocks of jade weighing hundreds of pounds called panaum by the Maories. Much of it is of the finest green colour and was worked into charms, knife-handles, &c. Dr. W. Buller exhibited a fine collection of Maori ornaments and clubs, or neeris, heitikas, and other native ornaments made of this stone.

Collections of Gems.—A regrettable dispersion of jewels and precious stones took place in May, 1886, when the famous collection formed by the late Henry Philip Hope, and exhibited at the South Kensington Museum for many years, was sold at auction. The Hope collection included the "Saphir Merveilleux" of Madame de Genlis's "Tales of the Castle;" the King of Kandy's cat's-eye, the largest known, having a diameter of 1½ inches; the Mexican Sun opal, carved with the head of the Mexican Sun God, and known since the sixteenth century; an enormous pearl, the largest known, weighing 3 ounces and measuring 2 inches in length; the aqua-marine sword-hilt, made for Murat, the King of Naples; and also many curious

diamonds, sapphires, emeralds, and several hundred unique and magnificent gems. Such a collection should have been preserved intact as a national possession.

In 1886 it was decided by the French Assembly that the Crown jewels, with the exception of the famous "Regent" diamond, two of the Mazarins, and a few historic pieces reserved for the national museums, should be sold at public auction. These exceptions were made because it was feared that they would fall into the hands of Americans. The sale of this great historic collection took place in May, 1887. The forty-eight parcels were subdivided into one hundred and forty-six lots, and there were sixty-eight buyers; the sales to twelve of them brought over 100,000 francs each. The largest lot, the great corsage, which sold for 811,000 francs, was purchased by a single American firm, the largest buyer at the sale. The purchases of this firm amounted to 2,249,600 francs, or about 34 per cent of the entire sum realised; while as to quality the same firm obtained more than two-thirds of the finest gems, among them were three Mazarins; a pear-shaped rose brilliant weighing $24\frac{31}{32}$ carats, for 128,000 francs; a pear-shaped white brilliant weighing $22\frac{1}{2}$ carats, for 81,000 francs; a white brilliant weighing $28\frac{7}{16}$ carats, for 155,000 francs; and an oval brilliant weighing $18\frac{1}{32}$ carats, for 71,000 francs; or 435,000 francs for the four. All but one of their purchases were secured by private American customers. The great interest attached to this sale was due not only to the fact that many of the gems were of very fine quality, but also to their historic associations; the history of many of them could be traced back several hundred years.

The collection of antique gems, numbering three hundred and thirty-one pieces, formed by the late Rev. C. W. King, of Trinity College, England, the greatest of all writers on engraved gems, was sent to the United States for sale in 1881. This collection represents the summing up of Mr. King's vast knowledge, and none has ever been more thoroughly studied. His numerous writings mark an epoch in the study of this branch of archæology, and only the loss of his sight led him to part with his treasure. The growing interest and taste in archæological matters in the United States induced him to send it there to be sold intact. In October, 1881, through the friendly mediation of Mr. Feuardent, it was purchased and presented to the Metropolitan Museum of Art by Mr. John Taylor Johnson, the president of the museum where it now remains. Near it will be placed the Sommerville collection. Mr. Maxville Sommerville, while spending the past thirty-two years of his life in Europe, Asia, and Africa, has collected cameos, intaglios, seals, and other historical gems, and as a result of his liberal expenditure of time and money he is to-day the owner of one of the most unique and valuable collections of engraved gems in the world. It numbers over one thousand five hundred specimens, including Egyptian, Persian, Babylonian, Etruscan, Greek, Roman, Aztec, and Mexican glyptic, or jewel carving art. All of these are represented by specimens of singular excellence, affording us a panoramic view of the achievements of civilised men in this direction. This remarkable collection, now at his home in Philadelphia, has been loaned to the Metropolitan Museum of Art, New York, where it will soon be placed on exhibition, and the public will be afforded every facility to study the beautiful achievements of the glyptic art.

Of greater antiquity and archæological value, because representing a period before gems were cut in the form of intaglios, is the collection of the Rev. W. Hayes Ward, consisting of 300 Babylonian, Persian, and other cylinders. Two hundred of these he himself collected in Babylon and its vicinity, and sold to the museum at a nominal figure. Since that time he has collected 100 more cylinders, many of them date from 2500 B.C. to 300 B.C., and are cut in lapis lazuli, agate, carnelian, hæmatite, chalcedony, jasper, sard, &c.

The death of Dr. Isaac Lea, of Philadelphia, in his ninety-fifth year, deprived the world of a great investigator in the field of precious stones. During the last twenty years of his exceptionally long and useful life, he devoted almost his entire time to studying the microscopic inclusions in gems and minerals, and the cabinet he left contains thousands of specimens of rubies, sapphires, chrysoberyls, tourmalines, garnets, quartz, &c., all of which he had subjected to the most rigid microscopic scrutiny, noting every interesting fact on the accompanying label. Only a small part of his work on this highly interesting subject has been published by the Philadelphia Academy of Sciences in two papers (in 1869 and 1876), but Dr. Lea made ample provision in his will for the publication of the remainder. His extensive collections of minerals and shells were bequeathed to the National Museum, and the gem collection to his daughter. Two months before his death the writer spent two hours with him examining a series of quartz inclusions, over which he worked with all the enthusiasm and brightness of youth.

One of the many benefits traceable to the New Orleans Exposition was the appropriation given to the National Museum for their exhibit. This was wisely expended by Prof. F. W. Clarke in the purchase of a complete series of precious stones, many of which, although not expensive, are still the finest in the United States, from an educational standpoint. Since the exposition, many fine specimens have been added by purchase and donation, especially the diamonds and pearls presented by the Iman of Muscat to President Buchanan, consisting of 138 diamonds and 150 pearls, all of good quality. The collection numbers about 1000 specimens, and embraces almost every known variety of precious stone, many of them very fine examples.

NOTICES OF BOOKS.

Picture-making by Photography. By H. P. Robinson. Second Edition, Revised. London: Hazell, Watson, and Viney, Limited.

This work is a difficult subject to handle in a scientific journal. The author says, doubtless with truth, that "art begins where chemistry and optics leave off." He says to his readers "buy your materials of those whose business it is to supply them, and confine your attention to the study of how to use them."

Against instantaneous photography the author raises an interesting objection, which is substantially that it shows us objects so as the eye never reveals them to us. Consequently they have an unnatural appearance. As he puts it, "the eye of the camera is the eye of man." A photograph of a moving object taken in *less* than that fraction of a second during which impressions remain on the retina is not true to nature as we see it. Still Mr. Robinson fully admits that instantaneous photography is valuable if not abused.

Report of the Fourth Indian National Congress held at Allahabad on the 26, 27, 28, and 29 December, 1888. London: Indian Political Agency.

This Report being in its character exclusively political, and having no bearing upon the interests of physical science, cannot come under the notice of the Chemical News.

Detection of Carbon Monoxide in the Air.—C. de la Harpe and F. Reverdin (*Chemiker Zeitung*) filter the air through slag-wool or cotton and pass it over pure dry iodic acid at 150° and then into a solution of starch-paste in distilled water. The monoxide is thus oxidised to dioxide, and the iodine liberated produces the usual blue colour with starch-paste.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

Sir,—In a recent criminal trial several chemical experts gave evidence as to processes for detecting arsenic and as to other chemical matters. From the detailed newspaper reports it does not appear that any one of these experts was asked by Counsel whether he was a Fellow or an Associate of the Institute of Chemistry.

The time is come when the Members of the Institute, especially the younger portion of them, expect to find their Association publicly recognised as a licensing body.

Would it, therefore, be too much to ask the Officials of the Institute if they are prepared to enquire whether in any recent trials chemical experts have *not* been requested to state their licensing qualifications before being allowed to give evidence; and, in the event of their not having been so requested, to publicly declare the illegality or inadvisability of the omission?—I am, &c.,

A.I.C.

August 19, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

New Element found along with Cobalt and Nickel.—G. Krüss and F. W. Schmidt.—The substance of this memoir has been already inserted.

Determination of Potassium.—Woussen.—The author does not weigh the potassium-platinum chloride as such, but reduces it by means of sodium formiate and determines the platinum separated.

The Electrolytic Separation of Iron.—Edgar F. Smith.—From the *American Chemical Journal.*

Separation of Cadmium from Zinc and Separation of Zinc, Nickel, Iron, and Manganese.—Ad. Carnot.—From the *Comptes Rendus.*

A Characteristic Reaction of Bismuth.—E. Léger (*Bulletin de la Soc. Chimique de Paris*).

Volumetric Determination of Stannous Compounds.—Adolf Jolles (*Chemiker Zeitung*).—Already inserted.

Determination of Fluorine in Compounds Decomposable by Sulphuric Acid.—H. Lasne.—From the *Bulletin de la Soc. Chimique de Paris*).

Method for Determining the Actual Nitrous Acid in Nitrites.—A. Vivier.—From the *Comptes Rendus.*

Recognition and Distinction of Gallic Acid and Tannin.—L. G. Rawson.—From the Chemical News.

Detection of Saccharine.—E. Börnstein and S. C. Hooker.—A controversy as to the trustworthiness of the method proposed by the former chemist.

Detection of Saccharine.—D. Lindo.—From the Chemical News.

Detection of Antipyrine and Antifebrine (Acetanilide).—D. Lindo.—From the Chemical News.

A New and Very Sensitive Reaction of Morphine.—Lister Armitage.—From the *Pharmaceutical Journal.*

Detection of Rhinanthine.—Dr. T. L. Phipson.—From the Chemical News.

On Kjeldahl's Process for the Determination of Nitrogen.—L. L'Hôte.—From the *Comptes Rendus.*

Determination of Alcohol.—B. Rœse (*Zeitschrift fur Angewandte Chemie*).—The author oxidises with permanganate in presence of sulphuric acid, adding the former reagent at once in excess.

Determination of Glycerin.—A number of methods taken from the *Comptes Rendus*, the *Chemiker Zeitung*, the *Journal of the Society of Chemical Industry*, and other journals.

Examination of Water for Dissolved Gases.—L. W. Winkler (*Berichte*).—The author oxidises an excess of manganous oxide to manganic oxide in presence of alkali by means of the oxygen dissolved in a known weight of water. The quantity of manganic oxide is next determined iodometrically.

Determination of Free and Semi-combined Carbonic Acid in Drinking or Industrial Waters.—Leo Vignon.—From the *Comptes Rendus.*

Detection of "Measles" in Sausages.—Schmidt Mülheim (*Deutsche Med. Zeitung*).—The author digests the sample with an excess of artificial gastric juice.

Examination of Butter.—G. Ambühl (*Chemiker Zeitung*) proposes, for determining the specific gravity of butter-fat at 100°, an apparatus closely resembling that of Soxhlet. For detecting artificial colouring-matters in butter, E. M. Martin proposes a method in the *Analyst.*

Examination of Vermicelli for Foreign Colours.—L. Cavedoni.—Already inserted.

Analysis of Crude Materials containing Tartaric Acid.—Goldenberg, Geromont, and Cie.—The authors reply to the critique of Von Lorenz, and, admitting his objections in case of chemically pure materials, they maintain that in case of lees and crude argols the original method of Goldenberg gives more accurate results than the modified method of Von Lorenz (*Chemiker Zeitung*).

Solubility of Paraffin with reference to its Determination.—Br. Pawlewski and Jak. Filemonowicz.—1 part by weight of paraffin requires for its solution 3856·2 parts of glacial acetic acid. One volume of commercial petroleum dissolves in 8 to 16 vols. of glacial acetic acid, 1 vol. of green oils in 30 to 60, and 1 of petroleum residues in 20 to 50 volumes. Vaseline, ceresine, and ozokerite, like paraffin, are almost insoluble (*Berichte*).

Determination of Neutral Fats.—Max Gröger (*Zeit. Angew. Chemie*).—To obtain accurate results a decided excess of caustic potash must be used for saponification. To 5 grms. fat must be taken such an excess of alkali that not less than 5 c.c. of semi-normal acid are needed for titrating back.

The Detection of Sugar in the Commercial Extract of Logwood.—Otto Schweissinger.—Already inserted.

Determination of Alcohol in Chloroform.—H. Hager.—The author shakes up the sample with glycerin which has been diluted with one-fourth to one-third of its volume of water.

Detection of Antefebrine in Phenacetine.—J. Schröder (*Nederl. Tija. voar Pharm.*).—The author boils 0·5 grm. in 5 to 8 c.c. water, cools, and filters. The filtrate is boiled with dilute nitric acid to which a little potassium nitrite has been added; a few drops of nitric acid containing nitrous acid are added, and the liquid is boiled again. Pure phenacetine undergoes no change, but if 2 per cent of antifebrine are present there is distinct reddening.

Examination of Natural Oil of Bitter Almonds containing Hydrocyanic Acid.—Kremel (*Pharm. Post*).—The author heats with an excess of potassa in alcohol and titrates back with hydrochloric acid. Yellow crystalline benzoin separates out, and is collected, dried, and weighed. It should amount to 40 to 50 per cent of

the sample operated upon. Laurel oil containing hydrocyanic acid and nitrobenzol yield no benzoin.

Adulteration of Balsam of Tolu.—R. A. Cripps.—From the *Pharm. Journal.*

New Process for Determining Urea in Urine.—E. Pflüger and L. Bleibtreu.—This method will be given in detail as soon as possible.

Detection of Free Hydrochloric Acid in Gastric Juice with Methyl-violet.—According to F. Penzoldt and G. Kost (*Medicin Centralblatt*) this method succeeds often only if the gastric juice has been previously precipitated with a 10 per cent solution of tannin.

Detection of Sugar in Urine.—C. Schwarz (*Pharm. Zeitung*).—The author uses the phenylhydrazin test.

Determination of Globuline in Albuminiferous Urine.—D. Kamenski (*Diss. Petersburg* and *Chem. Centralblatt*).—The author modifies Hammarsten's process by saturating the undiluted urine with magnesium sulphate.

Benzoyl Chloride as a Reagent for Cystine, Carbohydrates, and Diamines in Urine.—E. Baumann (*Zeit. Physiol. Chemie*).—Not adapted for useful abridgment.

Determination of Albumenoids with especial reference to Milk.—J. Sebelien (*Zeit. Physiol. Chemie*).—The author precipitates the albumenoids by Ritthausen's process and determines the nitrogen in the precipitate according to Kjeldahl.

Separation of Cocaine from Animal Remains.—U. Mussi (*Orosi*).—The comminuted substance is mixed with 2 parts of alcohol at 90 per cent, acidulated distinctly with hydrochloric acid, digested for a long time at 60° in a reflux condenser, repeating this process with fresh alcohol, evaporating the filtrates almost to dryness at 50° to 60°, taking up the residue with water, shaking out the solution two to three times with ether, precipitating the residual aqueous concentrated liquid with baryta, and extracting repeatedly with ether. The ethereal solution is evaporated in a vacuum and the residue tested for cocaine.

Studies on the Chemico-legal Demonstration of Blood.—A. Klein (An Inaugural Dissertation).—A bulky memoir which does not admit of useful abstraction.

New Reaction for Carbon Monoxide in Blood.—Kuniyosi Katayama (*Chem. Centralblatt*).—Blood containing carbonic oxide after the addition of orange-coloured ammonium sulphide and acetic acid at 30 per cent, takes a fine light red colour, whilst normal blood appears greenish grey or reddish greenish grey.

The Atomic Weight of Copper.—T. W. Richards (*American Academy of Arts and Sciences* and *American Chemical Journal*).—The author's first series of experiments lead to the mean value 63·628 (Ag=108) or 63·437 (Ag=107·675). The mean of the two last series shows a value of 63·450 (Ag=107·65).

Journal de Pharmacie et de Chimie.
Vol. xix., No. 10.

Detection of Nitrates in Potable Waters.—S. C. Hooker.—To 2 c.c. of the water the author adds 4 c.c. of pure strong sulphuric acid, and when the mixture is cold a small quantity of carbazol in sulphuric acid. A green colouration indicates the presence of nitric acid.

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NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS *will be published on Friday, September 20th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.*

Advertisements for this Number should reach the Office not later than Wednesday, the 18th prox.

THE CHEMICAL NEWS.

Vol. LX. No. 1554.

ON THE CAVENDISH EXPERIMENT.*

By C. V. BOYS, A.R.S.M., F.R.S.,
Assistant Professor of Physics at the Normal School of Science, South Kensington.

(Concluded from p. 100).

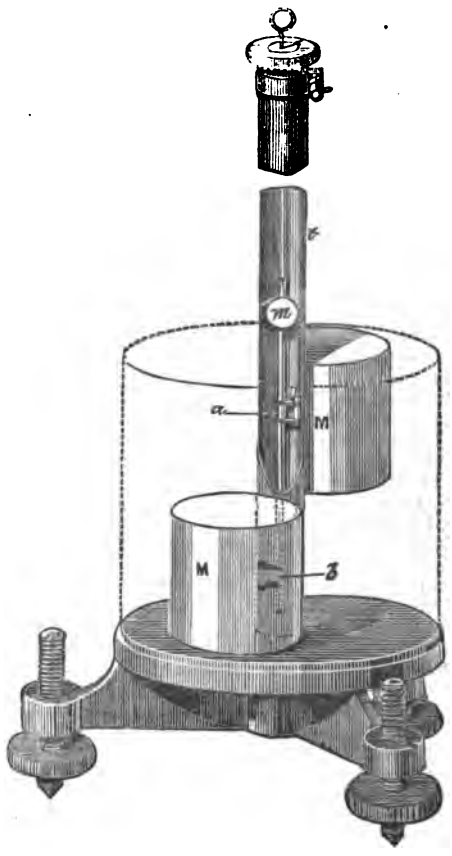
Having found that with apparatus no bigger than an ordinary galvanometer it should be possible to make an instrument far more sensitive than the large apparatus in use heretofore, it is necessary to show that in practice such a piece of apparatus will practically work, and that it is not liable to be disturbed by the causes which in large apparatus have been found to give so much trouble.

I have made two instruments, of which I shall only describe the second, as that is better than the first both in design and in its behaviour.

The construction of this is made clear by the figure. To a brass base provided with levelling screws is fixed the vertical brass tube, *t*, which forms the chamber in which the small masses *a b* are suspended by a quartz fibre from the pin at the upper end. These little masses are cylinders of pure lead 11·3 m.m. long, and 3 m.m. in diameter, and the vertical distance between their centres is 50·8 m.m. They are held by light brass arms to a very light taper tube of glass, so that their axes are 6·5 m.m. from the axis of motion. The mirror, *m*, which is 12·7 m.m. in diameter, plane and of unusual accuracy, is fastened to the upper end of the glass tube by the smallest quantity of shellac varnish. Both the mirror and the plate-glass window which covers an opening in the tube were examined and afterwards fixed with the refracting edge of each horizontal, so that the slight but very evident want of parallelism between their faces should not interfere with the definition of the divisions of the scale. The large masses, M M, are two cylinders of lead 50·8 m.m. in diameter, and of the same length. They are fastened by screws to the inside of a brass tube, the outline of which is dotted in the figure, which rests on the turned shoulder of the base so that it may be twisted without shake through any angle. Stops (not shown in the figure) are screwed to the base, so that the actual angle turned through shall be that which produces the maximum deflection. A brass lid, made in two halves, covers in the outer tube and serves to maintain a very perfect uniformity of temperature in the inner tube. Neither the masses, M M, nor the lid touch the inner tube. The period of oscillation is eighty seconds.

With this apparatus placed in an ordinary room with draughts of air of different temperatures, and with a lamp and scale such as are used with a galvanometer, the effect of the attraction can easily be shown to a few, or, with a lime-light, to an audience. To obtain this result with apparatus of the ordinary construction and usual size is next to impossible, on account chiefly of the great disturbing effect of air currents set up by difference of temperature in the case. The extreme portability of the new instrument is a further advantage, as is evident when the enormous weight and size of the attracting masses in the ordinary apparatus are considered.

However, this result is only one of the objects of the inquiry which I have now the honour to submit to the Royal Society. The other object which I had in view was to find whether the small apparatus, besides being more sensitive than that hitherto employed, would also be more free from disturbances and so give more consistent results. With this object I have placed the apparatus in a long narrow vault under the private road between the Museum and the Science Schools. This is not a good place for experiments of this kind, for when a cab passes overhead the trembling is so great that loose things visibly move; however, it is the only place at my disposal that is in any degree suitable. A large drain pipe filled with gravel and cement and covered by a slab of stone forms a fairly good table. The scale is made by etching millimetre divisions on a strip of clear plate-glass 80 c.m. long. This is secured at the other end of the vault at a distance of 1053·8 c.m. from the mirror of the instrument. A telescope 132 c.m. long, and with an object-glass 5·08 c.m. in diameter, rests on V's clamped to the wall, with its object-glass 360 c.m. from the mirror. Thus any disturbance that the observer might produce if



nearer is avoided, and at the same time the field of view comprises 100 divisions. While the observer is sitting at the telescope he can by pulling a string move an albo-carbon light mounted on a carriage so as to illuminate any part of the scale that may happen to be in the field of the telescope. The white and steady flame forms a brilliant background on which the divisions appear in black. The accuracy of the mirror is such that the m.m. divisions are clearly defined, and the position of the cross-wire (a quartz fibre) can be read accurately to one-tenth of a division. This corresponds to a movement of the mirror of almost exactly one second of arc.

The mode of observation is as follows:—When all is quiet with the large masses in one extreme position, the position of rest is observed and a mark placed on the scale. The masses are moved to one side for a time and then replaced, which sets up an oscillation. The reading of every elongation and the time of every transit of the

* Extracts from a Paper read before the Royal Society, June 20, 1889.

Elongation.	Amplitude.	Decrement.	True position of rest.	Time of transit of 36·69. h. m. s.	Correction for transit of true position of rest.	True half period.
15·05			36·18	9 8 25·0	+0·08	
	38·15					80·2
53·20		0·805	36·20	9 45·5	−0·18	
	30·72					80·2
22·48		0·808	36·21	11 5·3	+0·24	
	24·80					80·0
47·28		0·807	36·20	12 25·8	−0·28	
	20·00					79 9
27·28		0·807	36·22	13 45·0	+0·41	
	16·12					80·1
43·40		0·805	36·21	15 6·0	−0·47	
	12·98					80·1
30·42		0·806	36·22	16 25·0	+0·63	
	10·46					79·5
40·88		0·802	36·24	17 46·0	−0·91	
	8·38					80·5
32·50		0·808	36·24	19 4·5	+1·13	
	6·77					79 8
39·27		0·808	36·26	20 27·0	−1·58	
	5·47					80·5
33·80		0·814	36·26	21 44·0	+1·94	
	4·45					
38·25						
		0·8066				80·08

mark are observed until the amplitude is reduced to three or four c.m. The masses are then moved to the other extreme position and the elongations and transits observed again, and this is repeated as often as necessary.

On the evening of Saturday, May 18th, six sets of readings were taken, but during the observations there was an almost continuous tramp of art students above, producing a perceptible tremor, besides which two vehicles passed, and coals were twice shovelled in the coal-cellar, which is separated from the vault in which the observations were made by only a four and a half inch brick wall. The result of all this was a nearly perpetual tremor, which produced a rapid oscillation of the scale on the cross-wire, extending over a little more than 1 m.m. This increased the difficulty of taking the readings, but to what extent it introduced error I shall not be able to tell until I can make observations in a proper place.

In spite of these disturbances, the agreement between the deflections deduced from the several sets of observations and between the periods is far greater than I had hoped to obtain, even under the most favourable conditions. In order to show how well the instrument behaved, I have copied from my note-book the whole series of figures of one set, which sufficiently explain themselves. (See Table above).

It will be noticed that the true position of rest is slightly rising in value, and this rise was found to continue at the rate of 0·36 c m. an hour during the whole course of the experiment, and to be the same when the large masses were in the positive or negative position. The motion was perfectly uniform, and in no way interfered with the accuracy of the experiments. It was due, I believe, to the shellac fastening of the fibre, for I find that immediately after a fibre has been attached this movement is very noticeable, but after a few days it almost entirely ceases; it is, moreover, chiefly evident when the fibre is loaded very heavily. At the time that the experiment was made the instrument had only been set up a few hours.

The mean decrement of three positive sets was 0·8011, and of three negative sets 0·8035. The observed mean period of three positive sets was 79·98, and of three negative sets, 80·03 seconds, from both of which 0·20 must be deducted as the time correction for damping.

The deflections obtained from the six sets of observations, taken in groups of three, so as to take into account the effect of the slow change of the position of rest, were as follows:—

From sets 1, 2, and 3	17·66 ± 0·01
„ 2, 3, and 4	17·65 ± 0·02
„ 3, 4, and 5	17·65 ± 0·02
„ 4, 5, and 6	17·65 ± 0·02

An examination of these figures shows that the deflection is known with an accuracy of about one part in two thousand, while the period is known to the four thousandth part of the whole. As a matter of fact the discrepancies are not more than may be due to an uncertainty in some of the observations of half a millimetre or less, a quantity which, under the circumstances, is hardly to be avoided.

The result of these experiments is complete and satisfactory. As a lecture experiment the attraction between small masses can be easily and certainly shown, even though the resolved force causing motion is, as in the present instance, no more than the 1·200,000th of a dyne, (less than 1·10,000,000 of the weight of a grain), and this is possible with the comparatively short half period of eighty seconds. Had it been necessary to make use of such half periods as three to fifteen minutes which have been employed hitherto, then, even though a considerable deflection were produced, this could hardly be considered a lecture experiment.

The very remarkable agreement between successive deflections and periods shows that an absolute measure made with apparatus designed for the purpose, but on the lines laid down above, is likely to lead to results of far greater accuracy than any that have been obtained. For instance, in the original experiment of Cavendish there seems to have been an irregularity in the position of rest of one-tenth of the deflection obtained, while the period showed discrepancies of five to fifteen seconds in seven minutes. The experiments of Baily made in the most elaborate manner were more consistent, but Cornu was the first to obtain from the Cavendish apparatus results having a precision in any way comparable to that of other physical measurements. The three papers published by him in the *Comptes Rendus* of 1878, referred to above, contain a very complete solution of some of the problems to which the investigation has given rise. The agreement between the successive values, decrement, and period is much the same that I have obtained, nevertheless the means of the summer and of the winter observations differ by about 1 per cent.

I have not referred to the various methods of determining the constant of gravitation in which a balance, whether with the usual horizontal beam or with a vertical beam on the metronome principle, is employed. They are essentially the same as the Cavendish method, except that there is introduced the friction of the knife-edges and the unknown disturbances due to particles of dust at these points, and to buoyancy, without, in my opinion, any compensating advantage. However, it would appear that if the experiment is to be made with a balance the considerations which I have advanced in this paper would point to the advantage of making the apparatus small, so that attracting masses of greater proportionate size may be employed, and the disturbance due to convection reduced.

It is my intention, if I can obtain a proper place in which to make the observations, to prepare an apparatus specially suitable for absolute determinations. The scale will have to be increased, so that the dimensions may be

determined to a ten-thousandth part at least. Both pairs of masses should, I think, be suspended by fibres or by wires, so that the distance of their centres from the axis may be accurately measured, and so that in the case of the little masses the moment of inertia of the beam, mirror, &c., may be found by alternately measuring the period with and without the masses attached. The unbalanced attractions between the beam, &c., and the large masses, and between the little masses and anything unsymmetrical, about the support of the large masses, will probably be more accurately determined experimentally by observing the deflections when the large and the small masses are in turn removed, than by calculation.

If anything is to be gained by swinging the small masses in a good Sprengel vacuum, the difficulty will not be so great with apparatus made on the scale I have in view, *i.e.*, with a beam about 5 c.m. long, as it would with large apparatus. With a view to reduce the considerable decrement, I did try to maintain such a vacuum in the first instrument, in which a beam 1·2 c.m. long was suspended by a fibre so fine as to give a complete period of five minutes, but though the pump would click violently for a day perhaps, leakage always took place before long, and so no satisfactory results were obtained.

With an apparatus such as I have described, but arranged to have a complete period of six minutes, it will be possible to read the scale with an accuracy of one ten-thousandth of the deflection, and to determine the time of vibration with an accuracy about twice as great.

NOTE ON A NEW CRYSTALLINE HYDRATE OF THALLIC OXIDE.

By DOUGLAS CARNEGIE, M.A.

When determining sulphur in galena by the potash and nitre-fusion method I have frequently found that considerable quantities of "red lead" are formed if the fusion be long continued, or if the vessel in which the fusion takes place be left uncovered. The excess of oxygen in the "red lead" above that required by the formula PbO was variable, showing increase with time of fusion. This observation led me to attempt the formation of PbO_2 from litharge by long-continued fusion of the latter with potash and nitre. Not only was this attempt successful, but I soon found that nitre is not essential for this oxidation; the oxygen of the air will do equally well.

Litharge added slowly to fusing potash dissolves in large quantity, and if the resulting potassium plumbite be strongly heated for some time, freely exposed to the air the while, it is completely oxidised to potassium plumbate. On extracting the cooled fuse with water, a colourless, strongly oxidising solution is obtained which has properties greatly resembling those of an alkaline hypochlorite solution. If such a solution is treated with excess of dilute HClAq, chlorine is evolved; if a small quantity of litharge is suspended in it and the mixture then warmed, the litharge is changed to peroxide of lead, while potassium plumbite remains in solution; if treated with $MnSO_4Aq$, a dark brown precipitate of manganese peroxide is formed.

If the solution is *carefully neutralised* with dilute H_2SO_4Aq, a brown precipitate of PbO_2H_2O is thrown down. This is probably the same hydrate that Becquerel obtained at the positive electrode on electrolysing strongly alkaline solutions of lead salts (*Ann. Chem. Phys.* [3], viii., p. 405). If the H_2SO_4Aq be added rapidly and in excess, chlorine is evolved and $PbSO_4$ is precipitated. The appearance of chlorine in this case I would attribute to the presence, in commercial potash, of considerable quantities of chlorides, which, as is well known, by interacting with H_2SO_4 in the presence of a peroxide, give rise to free chlorine.

Now the "ornithorhynchus of the elements"—thallium—shows many analogies with lead, and it occurred to me that still other analogies might be added to the list if the behaviour of the lower oxidised compounds of thallium, when subjected to the action of molten potash, were investigated. The more sanguine was I on account of recent experiments referred to in the Chemical Society's Abstracts for 1888; these experiments, though failing in the actual isolation of a peroxide of thallium (TlO_2), nevertheless, according to the author, clearly pointed to the existence of such an oxide. But as a matter of fact no analogy exists between thallium and lead in this connection.

In my experiments I made hydrated thallic sesquioxide (prepared by Messrs. Harrington, of Cork) my starting-point. If this be dropped slowly and with constant stirring into molten potash,* a small quantity dissolves, and a clear yellow fuse, which probably contains a potassic thallite, results. This salt is, however, very unstable, for if the molten potash be allowed to cool as soon as it has dissolved the maximum quantity of thallic oxide, and the fuse then extracted with water, decomposition ensues and a red-brown precipitate of hydrated thallic sesquioxide separates. This behaviour is pretty much what one would anticipate on recalling the position of thallium in Group III. of Mendeleeff's periodic classification, and the well-founded generalisation in connection therewith, viz., that as the atomic weights of the elements of a group increase, the acidic nature of the corresponding oxides decreases.

If, however, the heating of the clear yellow fuse obtained as above be long continued, beautiful crystalline plates separate. After cooling, the fuse is extracted with water and the crystals washed repeatedly by decantation, first with boiling water till free from adhering potash, and finally with alcohol. The crystals, dried at 100°, give off a mere trace of chlorine when distilled with HClAq (*vide* next paragraph), and contains 80·38 per cent of thallium. The value given is a mean of several concordant results obtained—

(1) By previous reduction to thallous salt, followed by titration with permanganate in presence of a sufficiency of dilute HClAq;

(2) By previous reduction to thallous salt, followed by precipitation of thallous iodide, which was then collected on a tared filter;

(3) By a new volumetric iodometric method for the direct determination of thallium in thallic salts, the details of which I hope to communicate as soon as I shall have completed a more thorough test of its accuracy and general applicability.

The substance is evidently $Tl(OH)_3$ or $Tl_2O_3.3H_2O$, which requires 80 per cent thallium. It it extremely light and forms a brown glistening mass composed of microscopic and exceedingly regular hexagonal plates transmitting yellow light. It is easily soluble in dilute HClAq and H_2SO_4Aq, but generally slight reduction to thallous salt occurs during solution (see *ante*). It is an exceedingly stable hydrate, and is unaffected by exposure to a temperature of 340° C. In this last respect the new hydrate (hydroxide?) contrasts strongly with the only other hydrate of thallium which has up to the present been recognised, viz., $Tl_2O_3.H_2O$; for, according to Carnelley (*Chem. Soc. Journ. Trans.*, 1888), $Tl_2O_3.H_2O$ begins to lose water at 100°, and is completely dehydrated at 230°.

It is interesting to note in this connection that aluminium—the first member of the sub-group of Group III. containing thallium—also forms a crystalline hydrate which loses its water only at a red heat. This hydrate has the composition $Al_2O_3.3H_2O$ or $Al(OH)_3$ (Becquerel "Ency. Chim.," iii., p. 190).

Gonville and Caius College,
Cambridge.

* The fusions were always conducted in a nickel dish which had been internally superficially oxidised (blackened) through long-continued contact with molten potash at high temperature. Nickel always superior to silver for fusions in air, acquires, I find, a vast superiority when thus "protected."

NOTE ON A NEW ALKALOID.*

By JOHN TSAWOO-WHITE.

In extracting in a poisoning case some food forwarded by the District Superintendent of Police, Bassein, by Otto-Stas's method for alkaloids, an amorphous substance was obtained, giving a purple colour with sulphuric acid and oxidising agents like potassium chromate and manganese dioxide. This reaction is supposed to be peculiar to strychnine and curarine, but this substance differs in some respects from these alkaloids. It is a slightly yellowish substance, amorphous, almost tasteless, and not bitter. It dissolves in water, alcohol, and in ether. Its solution in water is not alkaline, giving precipitates with iodine in potassium iodide with Meyer's reagent and with phosphomolybdic acid. It gives no reaction with nitric acid, and none with ferric chloride.

When I showed this substance and its strychnine-like reaction to Dr. Romanis, he tried the action of gold and platinum chlorides on it. Gold chloride gives a white precipitate which decomposes on standing, as it becomes dark coloured. It gives a precipitate of acicular crystals with platinum chloride.

It is a pity that so little of the substance could be obtained in a case like this, that no definite conclusion as to the nature of this probably alkaloidal substance can be drawn. The only thing that can be done is to record it so that, might we stumble on it again unawares, it would be no longer again elusive.

In the last report, just published, of the Chemical Examiner to Government, Burma, is given a short account of this substance.

Rangoon, July 30, 1889.

SPECIFIC VOLUME OF CAMPHOR AND OF BORNEOL DETERMINED WITH PROXIMATE ACCURACY.

By MITSURU KUHARA, Ph.D.

The materials employed in the experiments were ordinary commercial camphor and borneol, purified by repeated sublimation. Their melting- and boiling-points† were found to be as follows:—

	Melting-point.	Boiling-point.
Camphor	177·7°	205·3°
Borneol	—	209·7°

In these determinations a number of experiments were repeated, and in each necessary corrections were made.

The determination of the specific gravity of liquid camphor and of liquid borneol was made with the use of a cylindrical specific gravity bottle of a small size, whose capacity had carefully been ascertained by filling it with boiled distilled water. Either the camphor or the borneol was fused in a long cylindrical vessel over the paraffin-bath, and the specific gravity bottle and its stopper, tied separately with platinum wire, were both introduced into this cylindrical vessel and heated together with the melted camphor or borneol. As the boiling point of the liquid camphor and of the liquid borneol is always found a few degrees higher than that of the vapour, the moment the temperature of the liquid reached 205·3° or 209·7° (boiling-points of their vapours), the stopper was instantly closed and the bottle filled with the liquid was taken out, cooled, and weighed. These experiments were conducted under a higher barometric pressure than the normal, all the measurements being made by means of the corrected thermometer. The specific gravity was calculated according to the following formula referring to the water of 4°.

$$\text{Specific gravity} = \frac{W}{V(1+3\beta(T-t)}$$

W = Weight of the liquid camphor or borneol at T.
T = Boiling-point of camphor or borneol.
V = Volume of water at t (or the capacity of the bottle at t).
t = Temperature when the bottle filled with water was weighed.
3β = Coefficient of the cubical expansion of glass = 0·0000254.

I. *Experiments on Camphor*, $C_{10}H_{16}O$.

The following three experiments were performed with a bottle of the capacity of 6·28114 c.c. at 30·5°.

1. Camphor in the bottle weighed 5·1304 grms. at 205·3°.
2. " " " 5·1089 " "
3. " " " 5·1189 " "

The fourth experiment was performed with a bottle of the capacity of 2·98632 c.c. at 40·5°.

4. Camphor in the bottle weighed 2·4252 grms. at 205·3°.

Seven more experiments were performed with a bottle of the capacity of 2·74518 c.c. at 40·5°.

5. Camphor in the bottle weighed 2·2400 grms. at 205·3°.
6. " " " 2·2470 " "
7. " " " 2·2405 " "
8. " " " 2·2330 " "
9. " " " 2·2355 " "
10. " " " 2·2290 " "
11. " " " 2·2315 " "

Specific gravity at 205·3° deduced according to the formula given above:—

1.	0·8131
2.	0·8097
3.	0·8113
4.	0·8087
5.	0·8125
6.	0·8147
7.	0·8127
8.	0·8100
9.	0·8109
10.	0·8085
11.	0·8094
Mean	0·8110

$$\text{Specific volume} = \frac{\text{Molec. wt.}}{\text{Spec. grav.}} = \frac{152}{0{\cdot}811} = 187{\cdot}42$$

II. *Experiments on Borneol*, $C_{10}H_{18}O$.

The experiments were performed with a bottle of the capacity of 2·74518 c.c. at 40·5°.

1. Borneol in the bottle weighed 2·2284 grms. at 209·7°.
2. " " " 2·2284 " "
3. " " " 2·2265 " "
4. " " " 2·2245 " "
5. " " " 2·2390 " "
6. " " " 2·2258 " "

Specific gravity at 209·7°.

1.	0·8082
2.	0·8082
3.	0·8075
4.	0·8071
5.	0·8120
6.	0·8073
Mean	0·8083

$$\text{Specific volume} = \frac{\text{Molec. wt.}}{\text{Spec. grav.}} = \frac{154}{0{\cdot}8083} = 190{\cdot}5$$

* Contribution from the Laboratory of the Chemical Examiner, Burma.

† In most text-books the melting and boiling-points of camphor are given to be 174° and 204°, respectively, and the boiling-point of borneol to be 212°.

	Found.			Calculated.	
	Kopp.	Ramsay.	Yoshida.	C=14 and 11; H=3·5; O=12·2 and 7·8.	C=11; H=5·5; O=12·2 and 7·8.
Benzene	95·8	95·9	—	86·0	99·0
Phenol	103·6	106·9	—	103·8	106·9
Benzylalcohol	123·7	—	—	121·8	128·8
Benzaldehyd	118·4	—	—	119·2	122·2
Ethyl benzoate	172·4—174·8	—	163·1*	162·0	174·0
Benzoic acid	126·9	—	—	127·0	130·0
Naphthalene	149·2	—	—	150·0	154·0

* This number was observed according to Ramsay's method by Mr. H. Yoshida, Science College, Imperial University of Tokio.

Specific volume of camphor and of borneol calculated with Kopp's values of the atomic volumes of carbon, hydrogen, and oxygen, supposing the former as a ketone and the latter as an alcohol, is found to be as follows:—

Camphor.

C_{10}	10 × 11 = 110
H_{16}	16 × 5·5 = 88
O	1 × 12·2 = 12·2
Specific volume	210·2

Borneol.

C_{10}	10 × 11 = 110
H_{18}	18 × 5·5 = 99
O	1 × 7·8 = 7·8
Specific volume	216·8

Thus it is seen that the calculated values are much greater than those found by experiments. Also the specific volume of benzene and of some of its derivatives calculated with Kopp's values is often found to be much greater than those obtained experimentally. In Watts's "Dictionary of Chemistry," 3rd Supplement, page 2126, the following statements are given:—"Lothar Meyer makes H=3, and Löschmidt C=14 and H=3·5; and by assuming that half the carbon atoms in benzene have the value 11 and the remainder the value 14, and that hydrogen has the constant value 3·5, we obtain a value for this hydrocarbon which is identical with the observed values." Thus:—

	Calculated.		Found.	
			Kopp.	Ramsay.
C_3	3 × 14 = 42	96	95·8	95·9
C_3	3 × 11 = 33			
H_6	6 × 3·5 = 21			

I tried to apply these values of carbon and hydrogen and Kopp's values of oxygen (12·2 and 7·8) to camphor and borneol, supposing each to consist of a closed chain of six carbon atoms, like benzene, and I found that the calculated specific volumes are almost concordant with those observed.

	Camphor.	
	Calculated.	Found.
C_3 = 3 × 14	187·2	187·42
C_7 = 7 × 11		
H_{16} = 16 × 3·5		
O = 1 × 12·2		

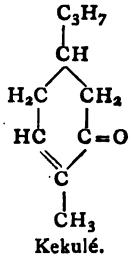
	Borneol.	
	Calculated.	Found.
C_3 = 3 × 14	189·8	190·5
C_7 = 7 × 11		
H_{18} = 18 × 3·5		
O = 1 × 7·8		

I tried further to compute the specific volumes of some of the benzene derivatives whose experimental numbers are already known, by applying similar methods of calculation to them (see Table above).

It thus appears that the numbers found by the new way of calculation agree better with the observed ones, in some cases, than with those calculated with Kopp's values.

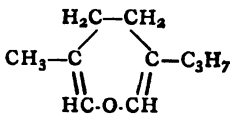
Now the principal formulæ for camphor suggested by different chemists are six in number, namely:—

I.*



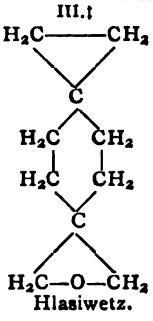
Kekulé.

II.†



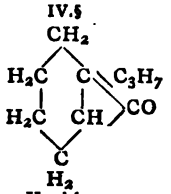
Victor Meyer.

III.‡



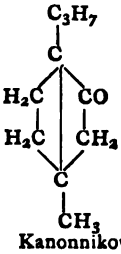
Hlasiwetz.

IV.§



Kachler.

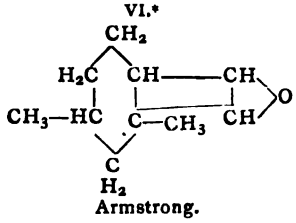
V.‖



Kanonnikow.

* *Ber. d. Deut. Chem. Gesell.*, vi., 929.
† *Ibid.*, iii., 116.
‡ *Ibid.*, iii., 540.
§ *Annalen d. Chem.*, clxv., 185.
‖ *Ber. d. Deut. Chem. Gesell.*, xvi., 3051.

VI.*



Armstrong.

If we suppose the above method of calculation to be true, there may exist in camphor a closed chain of six carbon atoms, and camphor itself may be a ketone, and then the formula I., IV., or V. may represent its constitution, as any one of the remaining formulæ would represent it as an oxide. Kanonnikow,† however, who determined the refraction equivalent of camphor and of its allied compounds by applying Bruhl's method, states that camphor has no double union between carbon atoms. Hence it may be concluded that one of the formulæ IV., and V. represent the constitution of camphor, and borneol is its corresponding alcohol. — *Journal of the Tokyo Chemical Society*, Vol. ix., No. 9.

ON KOBELLITE FROM OURAY, COL., AND THE CHEMICAL COMPOSITION OF THIS SPECIES.‡

By HARRY F. KELLER.

The sulphobismutites and sulphostibnites of the south-western part of Colorado have repeatedly formed the subject of mineralogical and chemical research. Genth, Kœnig, Hillebrand, and others have proved the occurrence there of a number of species already known from other localities, and have also described several new compounds of this class under the names of schirmerite, alaskite, and beegerite.

In the following pages I desire to give the description of a mineral possessing the composition—

$$2(Pb,Ag_2,Cu_2)S, (Bi,Sb)_2S_3,$$

and to show further that it is in all probability identical with the kobellite of Setterberg.

The material for this investigation was kindly supplied by my brother, Mr. Hermann A. Keller, of Pueblo, Col. It consisted of several beautiful specimens of an ore that had been taken from the Silver Bell mine, at Ouray, Col., by Mr. Philip Decker.

I have not been able to obtain any further information concerning the occurrence of the mineral, but consider it highly probable that it is closely analogous to that of alaskite described by Kœnig.§ Like this it is found associated with barite and chalcopyrite.

Physical Properties. — Massive. Structure, finely granular, inclining to fibrous; lustre, silky metallic; colour, bluish lead-grey; fracture, uneven; streak, iron-black; apparent hardness, 2·5—3; sp. gr., 6·334.

Chemical Deportment.—Upon heating, the mineral first decrepitates violently and then fuses. In the open tube, it gives off sulphurous acid and a sublimate of antimonious acid. Upon charcoal it yields a yellow incrustation, with a white non-volatile fringe and a metallic globule, which for the greater part is volatilised upon continued blowing.

The residue gives the reactions of iron and copper in the salt of phosphorous bead, and a button of metallic silver on cupellation. A crimson coating is obtained with potassium iodide and sulphur on charcoal.

Hydrochloric acid decomposes the compound with evolution of hydrogen sulphide, especially upon heating; the gangue material and chalcopyrite are left undissolved, while the silver passes into solution, from which it can be precipitated as chloride by diluting with water.

Chlorine, as well as nitric acid, exerts a powerful action upon it.

As the quantitative separation and estimation of the constituents presents some difficulties, I will briefly indicate the course of an analysis which was found to be best adapted to this end. A portion of the mineral was treated with nitric adid. When proper care is taken, the oxidation is completed in an hour's time. The excess of the acid was then removed upon the water-bath and the residue boiled with a solution of pure carbonate of soda. This treatment was continued until all the sulphuric acid, excepting the small quantity in the barite of the gangue, had passed in solution. The undissolved oxides and carbonates of the metals were then filtered off. The filtrate showed a bluish colour, and was found to contain small quantities of copper, antimony, and bismuth. These were precipitated by hydrogen sulphide, after acidifying with hydrochloric acid, and the sulphur then determined in the filtrate as barium sulphate. This was purified, after ignition, by heating with hydrochloric acid, then dissolving it in concentrated sulphuric acid, and re-precipitating it finally with water.

The separation of the metals was effected as follows:— The mixture of the oxides and carbonates, &c., was treated with nitric and tartaric acids, whereby only the gangue material ($BaSO_4$) remained undissolved. After the small quantity of sulphides before mentioned had likewise been taken up in the solution, the silver was precipitated as chloride in the cold; potassium hydrate was then added to the filtrate in excess, and hydrogen sulphide passed into it. The precipitate, consisting of the sulphides of all the metals except antimony, was filtered off, and the antimony determined in the liquid according to Bunsen's method as pentasulphide. The conversion of the pentasulphide into tetroxide served as a check, but gave invariably a slightly lower percentage.

The metallic sulphides were again oxidised with nitric acid, the latter removed by evaporation with sulphuric acid, and the remaining sulphates treated with dilute sulphuric acid (1 : 8) in the cold. In this manner the lead is separated from the other metals, but not completely, as the insoluble sulphate always contains small quantities of bismuth. It is therefore dissolved in warm potash solution, which leaves the oxide of bismuth with some lead, and these can then be separated readily by a renewed treatment with nitric and sulphuric acids.

In the solution containing the sulphates of copper, bismuth, iron, and zinc, the two first mentioned were precipitated as sulphides with hydrogen sulphide, filtered off, converted into the nitrates, and separated from each other with ammonia and ammonium carbonate. Zinc and iron were finally separated and determined by the usual methods.

In order to ascertain which of the metals enter into the composition of the mineral, one portion of the substances (Analysis II.) was dissolved in hydrochloric acid and the residue remaining analysed separately.

Although chlorine acts strongly upon the finely divided powder, I did not succeed in effecting a complete decomposition by its means. All the samples analysed were taken from different pieces of the ore.

	Analyses.					
	I.	II.	III.	IV.	V.	Mean.
S	18·37	—	18·46	18·33	18·39	18·39
Bi	27·97	28·51	28·68	28·46	—	28·40
Sb	7·19	7·25	7·91	7·84	—	7·55
Pb	36·11	36·08	36·25	36·20	—	36·16
Ag	3·22	3·39	3·30	3·32	—	3·31
Cu	2·43	2·26	2·91	2·76	—	2·59
Fe	1·31	1·35	1·69	1·65	—	1·50
Zn	0·50	0·37	0·41	0·31	—	0·39
$BaSO_4$, &c.	0·43	0·65	0·21	0·49	—	0·45
	97·53		99·82	99·36		98·74

* *Ber. d. Deut. Chem. Gesell.*, xi., 1698.

† *Ibid.*, xvi., 3051.

‡ Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

§ *Amer. Phil. Soc.*, June. 1881.

In No. II. the portion insoluble in hydrochloric acid was found to contain (after the chloride of silver had been removed by ammonia):—

Fe, 1·09 Cu, 1·12 Zn, 0·24

It seems therefore safe to assume* that the iron and an equivalent quantity of copper are present as chalcopyrite, and the zinc as sphalerite.

Now, deducting these, plus the gangue and the loss, the percentage composition calculated from the mean results is as follows:—

		Atomic ratio.		
S	= 17·76	0·5550		= 2·660
Bi	= 30·61	0·1457	0·2134	= 1·000
Sb	= 8·13	0·0677		
Pb	= 38·95	0·1881		
Ag	= 3·58	0·0166	0·2124	= 0·995
Cu	= 0·97	0·0077		
	100·00			

and the formula is therefore $2(Pb,Ag_2,Cu_2)S$, $(BiSb)_2S_3$. Since the atomic ratio of antimony† to bismuth is 1 : 2 the mineral may be considered as composed of 1 mol. of jamesonite with 2 mols. of cosalite.

The recent text books of mineralogy do not assign this formula to any mineral, nevertheless such a one has been known for a long time.

As kobellite, Setterberg‡ in 1839 first described a mineral from the cobalt mines of Hvena, in Sweden, the composition§ of which he found to be:—

S	= (18·61)
Bi	= 28·37
Sb	= 9·38
Pb	= 40·74
Fe	= 2·02
Cu	= 0·88
	100·00

Deducting from this the copper with the equivalent quantities of iron and sulphur, the atomic ratio are as follows:—

S	= 0·5506		= 2·581
Bi	= 0·1351	0·2133	= 1·000
Sb	= 0·0782		
Pb	= 0·1966	0·2187	= 1·025
Fe	= 0·0221		

that is, they are identical with those calculated from my analysis.

Setterberg states distinctly that the iron of his mineral was dissolved in hydrochloric acid, and must therefore be considered as belonging to it; another slight difference in the composition of the minerals from the two localities is the replacement of about one-twelfth of the lead by silver in that from Ouray.

In 1862 Rammelsberg published an analysis of some material from the Hvena mine; he found:—

S	= 18·22
Bi	= 18·60
Sb	= 9·46
As	= 2·56
Pb	= 44·25
Fe	= 3·81
Cu	= 1·27
Co	= 0·68
	98·85

After deducting 5·61 per cent of (FeCo)AsS and 3·67 per cent of $CuFeS_2$, he arrives at the formula—

$$Pb_3BiSbS_6.$$

In his "Mineralchemie" (p. 100), he gives an analysis of so-called kobellite from another locality (the name of which is not mentioned), and from this deduces the same formula.

He does not prove, however, that the analysis by Setterberg is incorrect, and it is more than likely that the material examined by him consisted of a mineral different from Setterberg's.

There are numerous instances of the occurrence of two different sulpho salts of similar appearance in the same vein, and even upon the same piece.

The re-investigation of alaskaite by Kœnig* was caused by it having been mistaken for cosalite from the same mine.

The specific gravity determinations also show a slight discrepancy; Setterberg found 6·29—6·32, while Rammelsberg's determination gave 6·145. That of the Ouray occurrence is 6·334.

In view of all these facts, I feel myself justified in retaining the name of kobellite for the mineral of the formula:—

$$2(Pb,Ag_2,Cu_2,Fe)S,\ (Bi_{(\frac{2}{3})}Sb_{(\frac{1}{3})})S_3,$$

and would suggest that another name be given to that to which the name has hitherto been applied, namely,—

$$Pb_3SbBiS_6.$$

In concluding, I desire to propose the name of lillianite for a mineral from the Lillian mine in Leadville, Col., described several years ago jointly by my brother and myself as a variety of kobellite. It possesses the composition $3(PbAg_2)S$, Bi_2S_3, and represents the bismuth mineral corresponding to boulangerite.

II. *Analysis of Megabasite from Bonita Mountain, near Silverton, Col.*

More than three years ago I received from Colorado, among other specimens, one which was labelled "gœthite." Some qualitative tests that were then performed upon it proved that it consists essentially of tungstic acid and manganous oxide. The occurrence has become quite well known since, but, as far as I am aware, no quantitative analysis of the material has been published. I may therefore be permitted to put the following on record:—

Sp. gr. = 6·780.

WO_3	= 74·24
MnO	= 21·09
FeO	= 2·06
CuO	= 0·11
MgO	= trace
SiO_2	= 2·13
	99·63

THE LUNDBERG CASE.†

By ELWYN WALLER, Ph.D.

SOME years ago (about 1880) Mr. Gustav Lundberg, agent for Messrs. Hoglund, of Sweden, contracted to supply to the Albany and Rensellaer Steel and Iron Co. a certain number of tons of Swedish pig-iron. In a letter appended to the contract was given the analysis of a sample of this iron (made in Sweden), and it was substantially agreed that the iron supplied should not be inferior in quality to that represented by the analysis. The iron was delivered, but the company claimed that it did not conform in quality to the contract, especially in the percentage of phosphorus. The result was a dispute as to payment, and consequently suit was brought. The case was tried about

* Chalcopyrite, when finely divided, is slightly acted upon by HCl.
† I have reason to believe that the antimony determinations I. and II. are a little too low.
‡ *Pogg. Ann.*, lv., 536.
§ Re-calculated with present atomic weights (Rammelsberg, *Mineralch.*, p. 100.

* *Proc. Amer. Philos. Soc.*, 1885, 211.
† From the *School of Mines Quarterly*, Vol. x., No. 3, April, 1889.

Analyst.	Sample.	Grms. taken.	Method of analysis.	*Phosphorus.* Furnace marks. NB GPH.	SBVE.	NB*B* BK.
S. B. Sharples ..	a	—	A MM	0·02	0·041	0·0055
J. B. Mackintosh ..	b	2	N MM	trace	0·01	0·01
,, ..	,,	5	,,	0·032	0·032	0·025
A. H. Elliott	c	5	Cl MM	trace	trace	0
,, ...	,,	10	N MM	0·0307	0·0223	0·028
,, ...	,,	10	A MM*	0·035	0·0223	—
E. B. Hills	d	—	A MM	0·027	0·033	0·022
S. C. Eaton	,,	1	Eggertz	0·016	0·0039	0·0039
J. M. Sherrerd ..	e	6—8	N MM	—	0·038, 0·041, 0·040, 0·0335	—
P. W. Shimer . ..	,,	3—4	N MM	—	0·039, 0·039	—
A. S. Bertolet . ..	f	5	N MM	0·048	—	—
J. M. Sherrerd ..	,,	6—8	N MM	0·0528, 0·0544, 0·0508	—	—
—	—	—	—	0·0491, 0·0499	—	—
A. S. McCreath ..	g	5—10	A Cit	0·0458, 0·0463, 0·0444	0·0391, 0·0382, 0·0391	0·0452, 0·0458, 0·0441
,, ..	,,	5	Cl Cit	0·0447	—	—
J. M. Sherrerd . ..	,,	5—7	N MM	0·048, 0·0475, 0·047	0·0424, 0·0413, 0·0367	0·045, 0·046, 0·0437
A S. McCreath ..	h	5—10	A Cit	0·0463, 0·0469, 0·0455	—	—
J. M. Sherrerd . ..	,,	6—8	N MM	0·048, 0·0486, 0·0467	—	—
A. S. McCreath ..	i	5	A Cit	0·0464, 0·0463, 0·0474	—	—
A. A. Blair	,,	10	N Cit	0·043	—	—
W. O. Wuth	,,	5	N MM	0·047, 0·047	—	—
J. M. Sherrerd . ..	,,	5—7	N MM	0·0475, 0·0479, 0·0467	—	—
A. S. McCreath ..	j	5—10	A Cit	0·048, 0·0469	—	—
,, ..	,,	5	Cl Cit	0·0474	—	—
A. A. Blair	,,	5	N Cit	0·044	—	—
W. O. Wuth	,,	5	N MM	0·048, 0·048	—	—
J. M. Sherrerd . ..	,,	6—8	N MM	0·0493, 0·0475, 0·0479	—	—
A. S. McCreath ..	k	5—10	A Cit	0·0435	—	0·0402
—	,,	5	Cl Cit	0·0446	—	0·0407
W. O. Wuth	,,	5	N MM	0·046, 0·046	—	0·044, 0·0438
J. M. Sherrerd . ..	,,	5—7	N MM	0·0446, 0·0431	0·0363, 0·0355	0·0413, 0·0403
A. H. Sherrerd and D. W. Humphreys	l	5	N MM	0·0425, 0·0419	0·03520, 0·358	0·0425, 0·0413, 0·0430
T. M. Drown	,,	5—8	N MM	0·0445, 0·0422, 0·0441	0·0336, 0·0345, 0·0344	0·0420, 0·0405, 0·0414
S. A. Ford	,,	4—10	N Cit	0·0456, 0·048	0·0394, 0·0396	0·040, 0·041
W. O. Wuth	,,	5	N MM	0·048	0·038	0·047
T. H. Garrett.. ..	,,	3—4	N Cit	0·049, 0·052, 0·052	0·042, 0·039, 0·044	0·040, 0·046, 0·049
A. S. Bertolet.. ..	,,	5	N MM	0·046	0·044	0·050
J. M. Sherrerd . ..	,,	6—8	N MM	0·053, 0·0527	—	0·0468, 0·0503

* Second method, Cairns' "Quant. Anal.," p. 82.

a year after before a jury, decided, appealed, and a new trial ordered, which finally took place in 1887. Numerous analyses of the iron were made by different chemists in the country, and the trials brought out voluminous and interesting testimony as to methods of analysis, the discrepancies to be expected from different analysts, the difference between different pigs from the same furnace, &c. Some of the points relating more especially to the questions of analytical chemistry involved have been here collected from the stenographic notes on the case, which were kindly placed at my disposal for this purpose by Mr. Everett P. Wheeler, one of the counsel for Mr. Lundberg. The notes, however, in some few respects were not absolutely complete, so that a few omissions in the record have been unavoidable.

In the tables of results the sets of samples are designated by letters. In some cases borings were sent to the analysts; in many others, however, certain pigs of the iron were taken to their laboratories, and each analyst took his own borings, so that where two or more analysts are credited in the tables with having had the same sample, they frequently had only borings from the same pigs.

The iron was from three different furnaces, presumably running uniformly, and the pigs from each furnace were designated by a set of letters cast into each pig. The marks were respectively NB GPH, SBVE, and NB*B* BK.

In the tables of results is incorporated a brief suggestion of the mode of analysis pursued.

Results for Phosphorus.

In the column headed Methods of Analysis the first letter indicates the solvent employed at the start. A signifies *aqua regia* or, at least, nitric acid with some addition of hydrochloric; N signifies nitric acid; and Cl chlorate of potash and hydrochloric acid. Succeeding these, MM indicates the use of the molybdate-magnesia method, and Cit the citric acid method. The methods will be more fully described later on.

Methods Used for the Determination of Phosphorus.

Amount Taken.—Most of the analysts used at least 5 grms. The amount, however, varied from one to ten.

Solution of the Iron.—The majority of the analysts seem to have used nitric acid alone, though in some cases it appeared that a little hydrochloric acid had been afterwards added, and in describing the method the witnesses had forgotten to mention it, as it was regarded by them as unimportant, the hydrochloric acid only being used occasionally to hasten the action. Three used *aqua regia* as their regular method. Messrs. Garrett, McCreath, and J. M. Sherrerd tried the use of other solvents than it had been their custom to use. No perceptible influence on the result ensued, though Dr. Wuth expressed a positive belief, founded on the observations of Stockmann (*Fres. Zeits.*, xvi., 172), that HCl could not be used in the solution of the iron without loss of phosphorus as PCl_5. On the other hand, several of the analysts declared, as the results of their own experience, that the use of some HCl

was admissible, all, of course, agreeing upon the necessity of the predominance of a strong oxidising agent.

Evaporation.—After effecting solution, evaporation to dryness necessarily followed, but in the heating of the evaporated mass to render the silica insoluble and to destroy carbonaceous material, the practice was very varied, both as to temperature and as to time. The widest difference was between heating for several hours (about ten) to 110° C. (Mackintosh), and heating for a short time to dull red heat (Wuth). Aside from these extremes the time varied from thirty minutes to three hours, the temperature from 120° to 165° C. Messrs. Blair and Wuth testified to dissolving in HCl after the first heating, and again evaporating to dryness.

To recover the small amount of iron, and possibly of phosphorus, which might have adhered to the silica, Dr. Drown ignited after filtering and treated with *aqua regia*; Messrs. Garrett and Blair expelled the silica by hydrofluoric acid, fused the residue with alkaline carbonate, and added the solution therefrom to the main solution. The other analysts did not testify to having taken any such precaution, and presumably in most cases it was omitted.

Further Treatment. — Beyond this point there was inevitably a divergence, according to the method to be pursued. Messrs. Ford, Garrett, Blair, and McCreath used the "citric acid method," or, as some called it, the "acetate method." The iron was reduced by alkaline sulphite, sulphuretted hydrogen passed through to remove arsenic if present, the solution filtered, boiled, and then a portion of the iron re-oxidised. For this purpose Messrs. Garrett and Blair used bromine; Messrs. Ford and McCreath used potassium chlorate. Then, after neutralising with ammonia and adding alkaline acetate, basic ferric acetate containing the phosphorus was precipitated by boiling. The precipitate was dissolved in hydrochloric acid, and citric acid added, followed by magnesium mixture and ammonia.

Both of the Messrs. Sherrerd passed H_2S through the filtrate from the silica to remove arsenic if present, and then re-oxidised the whole of the iron. Messrs. Mackintosh and Elliott reduced the iron as above described, re-oxidised a portion with potassium permanganate, and precipitated as for the "citric acid method," but carried the precipitate through by the molybdate-magnesia method (Cairns' second method).

Molybdate Precipitation.—There was a substantial agreement on all sides as to the necessity for effecting the molybdate precipitation in presence of a predominance of nitric acid and nitrates; as to the permissibility of the presence of hydrochloric acid and chlorides there was some difference of opinion and practice. As to the amount of molybdate reagent used, the time the mixture was allowed to stand, and the temperature at which it stood, there was a great diversity of practice. Mr. Eaton (who used the Eggertz method by request of one of the counsel, and took but 1 grm. of the iron in accordance with Eggertz's directions*) used 10 c.c. only. 25 c.c. was used by some other analysts, and 100 c.c. by several others. The mixtures were usually allowed to stand for precipitation over night, though some prolonged the standing to twenty-four or even forty hours. The temperature employed was sometimes the ordinary temperature of the laboratory, sometimes about 40° C.

Dilute molybdate solution, dilute acidified ammonium nitrate, or dilute nitric acid were used in washing the precipitate.

Magnesium Precipitation.—In some cases the molybdate precipitation had been so managed that the ammonia used for solution left behind a small amount of iron, so that some of the analysts, as a regular custom, passed hydrochloric acid through the filter-paper, and then added a small amount of citric acid or of Rochelle salt before adding the magnesium mixture.

Messrs. Drown, Mackintosh, and J. M. Sherrerd testified to allowing the ammoniacal solution to stand for some time in order to allow any silica, &c., to separate and to be filtered off before adding the magnesium mixture.

The amounts of magnesium mixture used ranged from 2 c.c. to 25 c.c. From 10 to 20 c.c. were most frequently used.

So far as the testimony went, the magnesium mixture prepared with the chloride (Gooch's formula) was invariably used.

The time allowed for the deposition of the precipitate varied from two or three hours to twelve or fifteen. The most common practice appeared to be allowing it to stand over night. The addition of alcohol to the ammonia solution used for washing was mentioned by several as their usual habit.

Testing the Precipitate.—In most cases, after the ignition of the precipitate and weighing, it was dissolved in acid, and the insoluble silica, if present, filtered off and its weight deducted. Where provision had not been previously made for the removal of arsenic, the solution was tested with sulphuretted hydrogen.

Mr. A. H. Sherrerd, by his assistant, Mr. D. H. Humphreys, carried through a blank ordinary analysis, and deducted the amount so found from the weight of the precipitate obtained.

(To be continued).

* *Vide* Chemical News, ii., 227.

OBITUARY.

PROFESSOR VICTOR EGGERTZ.

We regret to announce the death of the late Professor Victor Eggertz at the age of 72, who died at Stockholm last week.

He had, since 1883, been at the head of the School of Mines in Sweden, first at Fahlun and then at Stockholm, until a few years ago, when he retired, and his place was filled by Professor Richard Akermann.

Professor Eggertz was the inventor of the so-called colouration-test for analysing carbon in iron and steel, which has done so much good to all steel-making processes. This test was introduced into England as far back as 1860, when Mr. C. P. Sandberg gave a translation of Professor Eggertz's methods, and published them in the Chemical News, and there are now hardly any steel works in the country which do not use this rapid method of ascertaining the hardness of steel almost immediately when made, thus enabling assortments in the control and regularity of the product; and with the immense production of Bessemer and Siemens steel now going on it is easily conceived what a practical value this method of carbon estimation has had upon the steel production of the country.

CORRESPONDENCE.

VERMILION OR VERMILLION?

To the Editor of the Chemical News.

Sir,—Though of no particular importance, I would like to know if your numerous readers can explain why vermilion is sometimes spelt with one *l* and sometimes with two. Authorities in this respect differ. Ordinarily in English books we have "vermilion," which is also found in "Skeats's Dictionary," and, being allied to, or derived from, *vermeil*, we should suppose this to be the right spelling. This form is found in Frankland and Japp's "Inorganic Chemistry," and Watts, in "Fownes' Chemistry," uses both forms, "vermillion" in

the index, and "vermilion" in the body of the work. And "vermillion" is found in "Wagner's Chemical Technology," in Roscoe and Schorlemmer's "Treatise," and in Henry Watts's "Dictionary of Chemistry."—I am, &c.

J. Tsawoo-White.

Rangoon College, July 30, 1889.

THE BRITISH ASSOCIATION.

To the Editor of the Chemical News.

Sir,—I shall be obliged by your announcing in the next number of your journal that, at the Newcastle Meeting of the British Association there will be a joint discussion, by Sections B and G, of a paper to be read in the latter Section by Sir I. Lowthian Bell, F.R.S., President of Section B, on "Blast Furnace Practice."—I am, &c.,

Edward Rigg,
Recorder, Section G.

9, Royal Mint, E.C.,
August 30, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Moniteur Scientifique, Quesneville.
June, 1889.

On Alloys.—Professor W. Chandler Roberts-Austen, F.R.S.—From the *Journal of the Society of Arts.*

Arsenic in the Household.—Dr. W. Stokes.—From the Chemical News.

On the Same Subject.—From the Chemical News.

Existence of a Volatile Alkaloid in Pepper.—W. Johnstone.—From the Chemical News.

On Bumping during Ebullition.—C. Tomlinson.—From the Chemical News.

Some Curious Properties of Metals and Alloys.—Prof. W. Chandler Roberts-Austen.—From the Chemical News.

Determination of Fat in Milk and Cream, &c.—W. Schmid.—This paper will be noticed under the *Zeitschrift f. Anal. Chemie.*

Experiments on the Fermentation of Galactose, Arabinose, Sorbose, and some other Sugars.—W. Stone and B. Tollens.—Noticed under *Liebig's Annalen.*

Industrial Review and Patents.—A selection of specifications of chemical patents. Among these we find Dr. G. Krüss's method for obtaining pure nickel from the nickel of commerce or from its salts. The object of the patent is to separate pure nickel from the element which the author has provisionally designated as *x*. This object is effected by treating the solutions of nickel salts with basic ammonium oxalate, by melting with an excess of caustic soda the concentrated solution after having eliminated the oxalic acid, by taking up in a mineral acid or acetic acid the hydroxide which remained undissolved in the treatment with melting alkali, and treating it in heat with caustic soda or with a soluble oxalate in presence of organic acids capable of preventing the precipitation of alumina by the fixed alkalies, and by treating the mixture of Ni and *x* or of their salts by a metal more electropositive than nickel in a state of fine division.

New Process for the Industrial Production and the Partial Synthesis of Cocaine.—C. Liebermann and F. Giesel.—This paper, which does not admit of useful abstraction, is taken from the Berlin *Berichte.*

Improvement in the Manufacture of Potassium Chlorate.—J. Hamill.—From the *Journal of the Society of Chemical Industry.*

Decomposition of Potassium Chlorate by Heat in Presence of Manganese Peroxide.—Herbert McLeod.—From the *Journal of the Chemical Society.*

Industrial Society of Mulhouse.—Meeting of February 13th.—M. Noelting read a report on the work of M. Wiss, entitled "Summary of Novel Hypotheses on Chemistry in Space."

M. Galland presented a report on a memoir by M. Camille Schoen on the fixation of basic colouring-matters by means of tungstic acid.

M. Noelting read, on behalf of C. Krohn, a paper on the ethylenic ethers of the three amidophenols and the colouring-matters thence derived.

M. Noelting mentioned that in conjunction with M. Schwartz he had obtained triquinolylmethane on treating paraleucaniline or pararosaniline with glycerin, sulphuric acid, and picric acid.

Session of March 13, 1889.

M. Noelting communicated some novel results obtained on studying the nitro- and amido-toluquinoleins. He also read some historical notes on aniline-black.

Session of April 10, 1889.

Horace Kœchlin read a paper on the fixation of the St. Denis red. He also mentions that he has obtained good results in bleaching by the use of oxygenated water and magnesia.

M. Weber, of Winterthur, fixes chrome mordants in the cold with zincate of soda.

The Progress of Dyeing during the Second Half of 1888.—Dr. Erdmann (*Chemische Industrie*).—This paper does not admit of useful abstraction.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xix., No. 9.

The Fixation of Nitrogen in Slow Oxidations.—M. Berthelot.—Already noticed.

Fraudulent Panification. The Use of Copper Sulphate and Alum in the Production of Bread.—M. Bruylants (*Académie Royale de Médicine de Belgique.*—The author mentions the use of sodium, magnesium, ammonium carbonates, and of lime-water as of little importance, that of soap (!) as very rare, and that of zinc and copper sulphates and of alum as objectionable, giving a distinct character to the fermentation.

Variable Causticity of Phenol According to its Solvents.—P. Carles.—When pure phenol is dissolved in pure glycerin or strong alcohol its caustic properties are much reduced, but they return if water is added to the mixture, even in small proportions.

New Method of Determining Lithia by Means of the Fluorides.—A. Carnot.—Already noticed.

The Active Principles of Panama Bark.—MM Bielkin, Kobert, and Pachorufoff.—The saponine of Panama bark, which has been mistaken for a unitary principle, is a mixture of a highly poisonous compound, sapotoxine, and of a carbohydrate named lactosine. There is also present quillajic acid, a second poisonous body, having the characters of a glucoside. This acid is proposed as a reagent for detecting albumen in urine if the liquid has been slightly acidulated with acetic acid.

Detection of Mercury in Animal Liquids.—Prof. Merget (*Soc. Pharm. de Bordeaux*).—The author's process consists of three operations: treatment with nitric acid, precipitation of the mercury by copper, and detection of the metal by the action of its vapours upon a test-paper prepared with ammmoniacal silver nitrate.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. i., No. 11.

Preliminary Note on the Reactions of Dimethylaniline in Presence of Aluminium Chloride.—H. Giraud.—On treating dimethylaniline with ferric chloride either alone or mixed with aluminium chloride, all the ferric chloride is reduced, but there are formed merely red pitchy matters from which only traces of methylbenzidine can be extracted. If dimethylaniline is heated in an atmosphere of dry oxygen with pure aluminium chloride there is a rapid absorption of oxygen and a very large quantity of methylbenzidine is obtained.

Action of Hydrochloric Acid upon the Solubility of Cuprous Chloride.—R. Engel.—From 0° to 17° the solubility of cuprous chloride in hydrochloric acid increases very slightly with the temperature. Above 17° the solubility of cuprous chloride becomes greater.

Action of Hydrochloric Acid upon the Solubility of Lead Chloride.—R. Engel.—The author gives his results in the form of a table.

On the Hydrochlorates of the Chlorides in General.—R. Engel.—All the known hydrochlorates of chlorides are hydrated, the minimum quantity of water being 2 mols. to 1 mol. of hydrochloric acid. When hydrochloric acid combines at one and the same temperature in multiple proportions with a chloride the quantity of water increases by 2 mols. for 1 additional mol. of acid. No hydrochlorate of a chloride is insoluble, and the solubility of every such hydrochlorate is greater than that of the corresponding chloride, the hydrochlorate of the cupric chloride forming the sole exception. The increased solubility of certain chlorides in presence of hydrochloric acid is due to the formation of a hydrochlorate of a chloride.

Supplementary Note on the Colouring-matters derived from the Tetrabenzilic Ether of Benzidine. Albert Colson.—The colouring-matters extracted from the tetrazo-derivative of oxybenzylic benzidine have such an affinity for cotton that aqueous solutions of these colours can be totally decolourised by the introduction of cotton-yarn.

Use of Potassium Permanganate to Detect the Impurities of Alcohols.— P. Cazeneuve.— Permanganate shows if alcohol contains impurities, but it does not indicate their nature if they are agreeable aromas appreciated by the *gourmet* or volatile products which may exert a poisonous action. It does not inform the consumer if he is buying a good or a hurtful cognac, but it is of use to the pharmacist and the manufacturer of liqueurs who require a chemically pure alcohol as the basis of their preparations.

The Rapidity of Transformation of Metaphosphoric Acid.— Paul Sabatier.—This memoir does not admit of useful abstraction.

Use of Coloured Gases in Photography.— M. Delaurier.—M. Lippmann's researches on producing photographs having just proportions of light remind the author of some fruitless attempts of his own to obtain photographs in their natural colours by making use of three glasses, red, yellow, and blue. In these experiments he found that light, on passing an orange glass, gave an equality of photogenic action for objects of whatsoever nature.

Vol. i., No. 12.

Certain Combinations and Reactions of Nitric Oxide and of Nitrogen Peroxide with Some Anhydrous Chlorides.— A. Besson.— Nitrogen dioxide combines directly with liberation of heat with anhydrous antimony pentachloride. If rise of temperature is avoided there is no escape of gas. There is formed a crystalline mass having the composition $2SbCl_5NO_2$. Bismuth trichloride, gently heated in a current of nitric oxide, combines directly, forming a crystalline body. Nitrogen peroxide, if dry, combines directly with anhydrous antimony pentachloride to form a crystalline solid, $3SbCl_5,2NO_4$. Nitrogen acts also upon antimony terchloride, bismuth chloride, aluminium chloride, and ferric chloride. Upon sulphur chloride nitrogen does not exert an oxidising action, as it does upon the selenium chlorides.

The Oxidation of Triphenylmethane.— MM. Hanriot and O. St. Pierre.—The authors have discovered that the triphenylmethane which they had used in their researches was not quite pure, having been obtained from a benzene containing a little toluene.

Action of Potassium upon Triphenylmethane.— MM. Hanriot and Saint-Pierre.—The reaction of potassium upon triphenylmethane is the first instance of the direct substitution of a metal for the hydrogen of a hydrocarbon. The authors find that it may be extended to fluorene, anthracene, and naphthalin.

Vol. ii., No. 1.

Chemical Composition of the Rock Salt of Roumania.— M. Istrati.—The rock-salt contains from 98·052 to 99·894 of actual sodium chloride. It sometimes contains gases, a mixture of non-saturated hydrocarbons, and of oxygen sufficient to cause slight explosion. The author has never detected any compound ammonias, and the odour and flavour of petroleum found in some of the beds are easily expelled by exposure to the air, or by heat.

Determination of Nitric Nitrogen by Means of Ferrous Sulphate.—M. Bailhache.—Already noticed.

Vol. ii., No. 2.

Fixation of Nitrogen by the Bare Arable Soil with or without the Co-operation of Leguminous Plants. M. Berthelot.

The Fixation of Nitrogen in Slow Oxidations.—M. Berthelot.

The Origin of Bronze and the Sceptre of Pepi I., King of Egypt.—M. Berthelot.

The Reactions between Chromic Acid and Oxygenated Water.—M. Berthelot.

Continuation of the Same (Parts II. and III.).—M. Berthelot,

Formation-heat of Hydrogen Antimonide.— MM. Berthelot and Petit.

Combustion-heat of Carbon in its Different States.—MM. Berthelot and Petit.

Researches on the Thionic Series, Nos. I., II., and III.—M. Berthelot.—All these papers have been already noticed.

Journal fur Praktische Chemie.
Vol. xxxix., Nos. 10 and 11, 1889.

Researches from the Laboratory of the University of Freiburg.—This series includes papers by C. Willgerodt and H. Salzmann on the halogen-substituted toluols and benzoic acids; by Ad. Claus and H. Kunath on the bromotoluylic acids; by Ad. Claus and Nils Davidson on the chloroparatoluylic acids; and by K. Elbs and O. Hoermann on diphenoltrichloraethan and paradioxystilbene.

Calorimetric Investigations.— F. Stohmann.— A memoir by the author in conjunction with Cl. Kleber and H. Langbein on the method of combustion of organic substances in oxygen under high pressure. The paper, which is very extensive, cannot be reproduced without the accompanying plate.

Researches from the Laboratory of Prof. Alex. Saytzeff at Kasan ("On the Action of Iodethyl and Zinc upon Paraldehyd," by Woldemar Wwedensky).— The results of this reaction prove that, although the secondary butylic alcohol is formed it is in such trifling quantities that its origin must be ascribed to acetaldehyd, which, under the conditions present, is formed from paraldehyd.

MISCELLANEOUS.

Tuson Fund.—At a meeting of the Committee, held at the Royal Veterinary College on May 13, 1889, the accounts having been previously audited by Professors Attfield and Axe, the hon. secretaries were able to report that the total receipts amounted to £933 2s. 10d. Since that date a further sum of £60 17s. 9d. has been received, making a grand total of £994 0s. 7d. The balance sheet presented to the Committee showed that £96 10s. had been paid either directly to or on account of Mrs. Tuson, and that £17 10s. 1d. had been expended on printing, stationery, &c., leaving an available balance to date of £819 2s. 9d.; this, with the £60 17s. 9d. since received, gives a total of £880 0s. 6d. to be dealt with. The Committee decided that £750 should be expended in the purchase of an annuity for Mrs. Tuson, and that the balance should be expended for her benefit in such a manner as the hon. secretaries might think best. The hon. secretaries are now pleased to report that an annuity of £63 15s. has been bought for Mrs. Tuson in the Prudential Assurance Company, and, as authorised by the Committee, they have expended a further sum on her account of £56 0s. 1d., leaving a balance in hand of £74 0s. 5d. There still remains to be paid a small account for printing and postage, which will reduce this to about £70; this it is proposed to hand over to Mrs. Tuson. The hon. secretaries are requested by Mrs. Tuson to take this opportunity of offering to all those who have so kindly come to her assistance her most sincere and heartfelt thanks. — C. W. Heaton, Richard A. N. Powys, Hon. Secretaries.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Zinc Chloride—Can any reader tell me the addresses of the principal makers of this substance, its present market value, and if it is used *largely* in any manufacturing operation?—C. H. E.

Thermal and Electrical Units.—Can any reader direct me to a book giving particulars of the heats developed or required to effect certain reactions in chemistry, *e.g.*, the heat developed when Na_2 combines with O to form Na_2O, and the heat required to effect the separation again of the same bodies? A complete article upon the subject is what I want to find. I should also be glad of any information upon the best treatise upon electrical units and measurements, and the amount of electrical force required to effect electrical decompositons.—W. G. H.

TO CORRESPONDENTS.

Analyst.—Consult Dr. Lunge's books on the subject.

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SESSION 1889-90.

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THE CHEMICAL NEWS.

Vol. LX. No. 1555.

BRITISH ASSOCIATION
FOR THE
ADVANCEMENT OF SCIENCE.

Newcastle-upon-Tyne, 1889.

INAUGURAL ADDRESS OF THE PRESIDENT,

Professor W. H. Flower,
C.B., LL.D., F.R.S., F.R.C.S., Pres.Z.S., F.L.S., F.G.S.

It is twenty-six years since this Association met in Newcastle-upon-Tyne. It had then the advantage of being presided over by one of the most distinguished and popular of your fellow-townsmen.

Considering the age usually attained by those upon whom the honour of the presidency falls, and the length of time which elapses before the Association repeats its visit, it must have rarely happened that any one who has held the office is spared, not only to be present at another meeting in the town in which he has presided, but also to take such an active part in securing its success, and to extend such a hospitable welcome to his successor, as Lord Armstrong has done upon the present occasion.

The address which was delivered at that meeting must have been full of interest to the great majority of those present. It treated of many subjects more or less familiar and important to the dwellers in this part of the world, and it treated them with the hand of a master, a combination which always secures the attention of an audience.

When it came to my knowledge that in the selection of the President for this meeting the choice had fallen upon me, I was filled with apprehension. There was nothing in my previous occupations or studies from which I felt that I could evolve anything in special sympathy with what is universally recognised as the prevailing genius of this district. I was, however, somewhat reassured when reminded that in the regular rotation by which the equal representation in the presidential office of the different branches of science included in the Association is secured, the turn had come round for some one connected with biological subjects to occupy the chair, which during the past seven years has been filled with such distinction by engineers, chemists, physicists, mathematicians, and geologists. I was also reminded that the Association, though of necessity holding its meeting in some definite locality, was by no means local in its character, but that its sphere was co-extensive, not with the United Kingdom only, but with the whole of the British Dominions, and that our proceedings are followed with interest wherever our language is understood—I may say, throughout the civilised world. Furthermore, although its great manufacturing industries, the eminence of its citizens for their skill and intelligence in the practical application of mechanical sciences, and the interesting and important geological features of its vicinity, have conferred such fame on Newcastle as almost to have overshadowed its other claims to distinction in connection with science, this neighbourhood is also associated with Bewick, with Johnson, with Alder, Embleton, Hutton, Atthey, Norman, the two Hancocks, the two Bradys, and other names honoured in the annals of biology; it has long maintained a school of medicine of great repute; and there has lately been established here a natural history museum, which in some of its features is a model for institutions of the kind, and which, I trust, will be a means of encouraging in this town some of the objects the Association was designed to promote.

There can be no doubt that among the various methods by which the aims of the British Association (as expressed in its full title, the *advancement of science*) may be brought about, the collection and preservation of objects available for examination, study, and reference—in fact, the formation of what are now called "museums"—is one of very great practical importance; so much so, indeed, that it seems to me one to the consideration of which it is desirable to devote some time upon such an occasion as this. It is a subject still little understood, though, fortunately, beginning to attract attention. It has already been brought before the notice of the Association, both in presidential and sectional addresses. A committee of our members is at the present time engaged in collecting evidence upon it, and has issued some valuable reports. During the present year an association of curators and others interested in museums has been founded for the purpose of interchange of ideas upon the organisation and management of these institutions. It is a subject, moreover, if I may be allowed to mention a personal reason for bringing it forward this evening, which has more than any other occupied my time and my attention almost from the earliest period of my recollection, and I think you will agree with the opinion of one of my distinguished predecessors in this chair, "that the holder of this office will generally do better by giving utterance to what has already become part of his own thought than by gathering matter outside of its habitual range for the special occasion. For," continued Mr. Spottiswoode, "the interest (if any) of an address consists not so much in the multitude of things therein brought forward as in the individuality of the mode in which they are treated."

The first recorded institution which bore the name of museum, or temple, or haunt of the Muses, was that founded by Ptolemy Soter at Alexandria about 300 B.C.; but this was not a museum in our sense of the word, but rather, in accordance with its etymology, a place appropriated to the cultivation of learning, or which was frequented by a society or academy of learned men devoting themselves to philosophical studies and the improvement of knowledge.

Although certain great monarchs, as Solomon of Jerusalem and Augustus of Rome, displayed their taste and their magnificence by assembling together in their palaces curious objects brought from distant parts of the world—although it is said that the liberality of Philip and Alexander supplied Aristotle with abundant materials for his researches—of the existence of any permanent or public collections of natural objects among the ancients there is no record. Perhaps the nearest approach to such collections may be found in the preservation of remarkable specimens, sometimes associated with superstitious veneration, sometimes with strange legendary stories, in the buildings devoted to religious worship. The skins of the gorillas brought by the navigator Hanno from the West Coast of Africa, and hung up in the temple at Carthage, afford a well-known instance.

With the revival of learning in the Middle Ages, the collecting instinct, inborn in so many persons of various nations and periods of history, but so long in complete abeyance, sprang into existence with considerable vigour, and a museum, now meaning a collection of miscellaneous objects, antiquities, as well as natural curiosities, often associated with a gallery of sculpture and painting, became a fashionable appendage to the establishment of many wealthy persons of superior culture.

All the earliest collections, comparable to what we call museums, were formed by and maintained at the expense of private individuals; sometimes physicians, whose studies naturally led them to a taste for biological science; often great merchant princes, whose trading connections afforded opportunities for bringing together things that were considered curious from foreign lands; or ruling monarchs in their private capacity. In every case they were maintained mainly for the gratification of the possessor or his personal friends, and rarely, if ever,

associated with any systematic teaching or public benefit.

One of the earliest known printed catalogues of such a museum is that of Samuel Quickelberg, a physician of Amsterdam, published in 1565 in Munich. In the same year Conrad Gesner published a catalogue of the collection of Johann Kentmann, a physician of Torgau in Saxony, consisting of about 1600 objects, chiefly minerals, shells, and marine animals. Very soon afterwards we find the Emperor Rudolph II. of Germany busily accumulating treasures which constituted the foundations of the present magnificent museums by which the Austrian capital is distinguished.

In England the earliest important collectors of miscellaneous objects were the two John Tradescants, father and son, the latter of whom published, in 1656, a little work called "Musæum Tradescantianum; or, a Collection of Rarities Preserved at South Lambeth, neer London." The wonderful variety and incongruous juxtaposition of the objects contained in this collection make the catalogue very amusing reading. Under the first division, devoted to "Some Kindes of Birds, their Egges, Beaks, Feathers, Clawes, and Spurres," we find "Divers sorts of Egges from Turkie, one given for a Dragon's Egge;" "Easter Egges of the Patriarch of Jerusalem;" "Two Feathers of the Phœnix Tayle;" "The Claw of the bird Rock, who, as Authors report, is able to trusse an Elephant." Among "whole birds" is the famous "Dodar from the Island Mauritius; it is not able to flie, being so big." This is the identical specimen, the head and foot of which has passed through the Ashmolean into the University Museum of Oxford; but we know not what has become of the claw of the Rock, the Phœnix tayle, and the Dragon's egg. Time does not allow me to mention the wonderful things which occur under the head of "Garments, Vestures, Habits, and Ornaments," or the "Mechanick, Artificial Workes in Carvings, Turnings, Sowings, and Paintings," from Edward the Confessor's knit gloves, and the famous "Pohatan, King of Virginia's habit, all embroidered with shells or Roanoke," also still at Oxford, and lately figured and described by Mr. E. B. Tylor, to the "Cherry-stone, upon one side S. George and the Dragon, perfectly cut, and on the other side eighty-eight Emperours' faces;" or the other "cherry-stone, holding ten dozen of tortois-shell combs made by Edward Gibbons." But before leaving these private collections I cannot forbear mentioning, as an example of the great aid they often were in advancing science, the indebtedness of Linnæus in his early studies to the valuable zoological museums, which it was one of the ruling passions of several kings and queens of Sweden to bring together.

Upon the association of individuals together into societies to promote the advancement of knowledge, these bodies in their corporate capacity frequently made the formation of a museum part of their function. The earliest instance of this in our country was the museum of the Royal Society in Crane Court, of which an illustrated catalogue was published by Dr. Grew in 1681.

The idea that the maintenance of a museum was a portion of the public duty of the State or of any municipal institution had, however, nowhere entered into the mind of man at the beginning of the last century. Even the great teaching bodies, the Universities, were slow in acquiring collections; but it must be recollected that the subjects considered most essential to the education they then professed to give were not those which needed illustration from the objects which can be brought together in a museum. The Italian Universities, where anatomy was taught as a science earlier and more thoroughly than anywhere else in Europe, soon found the desirability of keeping collections of preserved specimens, and the art of preparing them attained a high degree of excellence at Padua and Bologna two centuries ago. But these were generally the private property of the professors, as were nearly all the collections used to illustrate the teaching of anatomy and pathology in our country within the memory of many now living.

Notwithstanding the multiplication of public museums during the present century, and the greater resources and advantages which many of these possess, which private collectors cannot command, the spirit of accumulation in individuals has happily not passed away, although usually directed into rather different channels than formerly. The general museums or miscellaneous collections of old are now left to governments and institutions which afford greater guarantee of their permanence and public utility, while admirable service is done to science by those private persons with leisure and means who, devoting themselves to some special subject, amass the materials by which its study can be pursued in detail either by themselves or by those they know to be qualified to do so; which collections, if they fulfil their most appropriate destiny, ultimately become incorporated, by gift or purchase, in one or other of the public museums, and then serve as permanent factors in the education of the nation, or rather of the world.

It would be passing beyond the limits of time allotted to this address, indeed going beyond the scope of the Association, if I were to speak of many of the subjects which have pre-eminently exercised the faculties of the collector and formed the materials of which museums are constructed. The various methods by which the mind of man has been able to reproduce the forms of natural objects or to give expression to the images created by his own fancy, from the rudest scratchings of a savage on a bone, or the simplest arrangement of lines employed in ornamenting the roughest piece of pottery, up to the most lovely combinations of form and colour hitherto attained in sculpture or in painting, or in works in metal or in clay, depend altogether on museums for their preservation, for our knowledge of their condition and history in the past, and for the lessons which they can convey for the future.

Apart from the delight which the contemplation of the noblest expressions of art must produce in all cultivated minds, apart also from the curiosity and interest that must be excited by all the less successfully executed attempts to produce similar results, as materials for constructing the true history of the life of man, at different stages of civilisation, in different circumstance of living, and in divers regions of the earth, such collections are absolutely invaluable.

But I must pass them by in order to dwell more in detail upon those which specially concern the advancement of the subjects which come under the notice of this Association—museums devoted to the so-called "natural history" sciences, although much which will be said of them will doubtless be more or less applicable to museums in general.

The terms "*natural history*" and "*naturalist*" have become deeply rooted in our language, but without any very definite conception of their meaning or the scope of their application. Originally applied to the study of all the phenomena of the universe which are independent of the agency of man, natural history has gradually narrowed down in most people's minds, in consequence of the invention of convenient and generally understood and accepted terms for some of its various subdivisions, as astronomy, chemistry, geology, &c., into that portion of the subject which treats of the history of creatures endowed with life, for which, until lately, no special name had been invented. Even from this limitation botany was gradually dissassociating itself in many quarters, and a "naturalist" and a "zoologist" have nearly become, however irrationally, synonymous terms. The happy introduction and general acceptance of the word "biology," notwithstanding the objections raised to its etymological signification, have re-united the study of organisms distinguished by the possession of the living principle, and practically eliminated the now vague and indefinite term "natural history" from scientific terminology. As, how-

ever, it is certain to maintain its hold in popular language, I would venture to suggest the desirability of restoring it to its original and really definite signification, contrasting it with the history of man and of his works, and of the changes which have been wrought in the universe by his intervention.

It was in this sense that, when the rapid growth of the miscellaneous collections in the British Museum at Bloomsbury (the expansion of Sir Hans Sloane's accumulation in the old Manor House at Chelsea) was thought to render a division necessary, the line of severance was effected at the junction of what was natural and what was artificial; the former, including the products of what are commonly called "natural" forces, unaffected by man's handiwork or the impress of his mind. The departments which took cognisance of these were termed the "Natural History Departments," and the new building to which they were removed the "Natural History Museum."

It may be worth while to spend a few moments upon the consideration of the value of this division, as it is one which concerns the arrangement and administration of the majority of museums.

Though there is very much to be said for it, the objection has been raised that it cuts man himself in two. The illustrations of man's bodily structure are undoubtedly subjects for the zoologist. The subtile gradations of form, proportion, and colour which distinguish the different races of men, can only be appreciated by one with the education of an anatomist, and whose eye has been trained to estimate the value of such characters in discriminating the variations of animal forms. The subjects for comparison required for this branch of research must therefore be looked for in the zoological collections.

But the comparatively new science of "anthropology" embraces not only man's physical structure; it includes his mental development, his manners, customs, traditions, and languages. The illustrations of his works of art, domestic utensils, and weapons of war are essential parts of its study. In fact it is impossible to say where it ends. It includes all that man is or ever has been, all that he has ever done. No definite line can be drawn between the rudest flint weapon and the most exquisitely finished instrument of destruction which has ever been turned out from the manufactory at Elswick, between the rough representation of a mammoth, carved by one of its contemporary men on a portion of its own tusk, and the most admirable production of a Landseer. An anthropological collection, to be logical, must include all that is in not only the old British Museum, but the South Kensington Museum and the National Gallery. The notion of an anthropology which considers savages and prehistoric people as apart from the rest of mankind may, in the limitations of human powers, have certain conveniences, but it is utterly unscientific and loses sight of the great value of the study in tracing the gradual growth of our complex systems and customs from the primitive ways of our progenitors.

On the other hand, the division first indicated is as perfectly definite, logical, and scientific as any such division can be. That there are many inconveniences attending wide local disjunctions of the collections containing subjects so distinct yet so nearly allied as physical and psychical anthropology must be fully admitted; but these could only have been overcome by embracing in one grand institution the various national collections illustrating the different branches of science and art, placed in such order and juxtaposition that their mutual relations might be apparent, and the resources of each might be brought to bear upon the elucidation of all the others—an ideal institution, such as the world has not yet seen, but into which the old British Museum might at one time have been developed.

A purely "Natural History Museum" will then embrace a collection of objects illustrating the natural productions of the earth, and in its widest and truest sense should include, as far as they can be illustrated by museum specimens, all the sciences which deal with natural phenomena. It has only been the difficulties, real or imaginary, in illustrating them which have excluded such subjects as astronomy, physics, chemistry, and physiology from occupying departments in our National Natural History Museum, while allowing the introduction of their sister sciences, mineralogy, geology, botany, and zoology.

Though the experimental sciences and those which deal with the laws which govern the universe, rather than with the materials of which it is composed, have not hitherto greatly called forth the collector's instinct, or depended upon museums for their illustration, yet the great advantages of collections of the various instruments by means of which these sciences are pursued, and of examples of the methods by which they are taught, are yearly becoming more manifest. Museums of scientific apparatus now form portions of every well-equipped educational establishment, and under the auspices of the Science and Art Department at South Kensington a national collection illustrating those branches of natural history science which have escaped recognition in the British Museum is assuming a magnitude and importance which brings the question of properly housing and displaying it urgently to the front.

Anomalies such as these are certain to occur in the present almost infantile though rapidly progressive state of science. It may be taken for granted that no scientific institution of any complexity of organisation can be, except at the moment of its birth, abreast of the most modern views of the subject, especially in the dividing lines between, and the proportional representation of, the various branches of knowledge which it includes.

The necessity for subdivisions in the study of science is continually becoming more apparent as the knowledge of the details of each subject multiplies without corresponding increase in the power of the human mind to grasp and deal with them, and the dividing lines not only become sharper, but as knowledge advances they frequently require revision. It might be supposed that such revision would adjust itself to the direction taken by the natural development of the relations of the different branches of science, and the truer conceptions entertained of such relations. But this is not always so. Artificial barriers are continually being raised to keep these dividing lines in the direction in which they have once started. Difficulties of re-adjustment arise not only from the mechanical obstacles caused by the size and arrangements of the buildings and facilities for the allocation of various kinds of collections, but still more from the numerous personal interests which grow up and wind their meshes around such institutions. Professorships and curatorships of this or that division of science are founded and endowed, and their holders are usually tenacious either of encroachment upon or of any wide enlargement of the boundaries of the subject they have undertaken to teach or to illustrate; and in this way, more than any other, passing phases of scientific knowledge have become crystallised or fossilised in institutions where they might least have been expected. I may instance many European universities and great museums in which zoology and comparative anatomy are still held to be distinct subjects taught by different professors, and where, in consequence of the division of the collections under their charge, the skin of an animal, illustrating its zoology, and its skeleton and teeth, illustrating its anatomy, must be looked for in different and perhaps remotely placed buildings.

For the perpetuation of the unfortunate separation of palæontology from biology, which is so clearly a survival of an ancient condition of scientific culture, and for the maintenance in its integrity of the heterogeneous compound of sciences which we now call "geology," the faulty organisation of our museums is in a great measure responsible. The more their re-arrangement can be made to overstep and break down the abrupt line of

demarcation which is still almost universally drawn between beings which live now and those which have lived in past times, so deeply rooted in the popular mind and so hard to eradicate even in that of the scientific student, and the better it will be for the progress of sound biological knowledge.

But it is not of the removal of such great anomalies and inconsistencies which, when they have once grown up, require heroic methods to set them right, but rather of certain minor defects in the organisation of almost all existing museums which are well within the capacity of comparatively modest administrative means to remedy, that I have now to speak.

That great improvements have been lately effected in many respects in some of the museums in this country, on the Continent, and especially in America, no one can deny. The subject, as I have already indicated, is, happily, exciting the attention of those who have the direction of them, and even awakening interest in the mind of the general public. It is in the hope of in some measure helping on or guiding this movement that I have ventured on the remarks which follow.

The first consideration in establishing a museum, large or small, either in a town, institution, society, or school, is that it should have some definite object or purpose to fulfil; and the next is that means should be forthcoming not only to establish but also to maintain the museum in a suitable manner to fulfil that purpose. Some persons are enthusiastic enough to think that a museum is in itself so good an object that they have only to provide a building and cases and a certain number of specimens, no matter exactly what, to fill them and then the thing is done; whereas the truth is the work is only then begun. What a museum really depends upon for its success and usefulness is not its building, not its cases, not even its specimens, but its curator. He and his staff are the life and soul of the institution, upon whom its whole value depends; and yet in many—I may say most of our museums—they are the last to be thought of. The care, the preservation, the naming of the speciments are either left to voluntary effort—excellent often for special collections and for a limited time, but never to be depended on as a permanent arrangement—or a grievously undersalaried and consequently uneducated official is expected to keep in order, to clean, dust, arrange, name, and display in a manner which will contribute to the advancement of scientific knowledge, collections ranging in extent over almost every branch of human learning, from the contents of an ancient British barrow to the last discovered bird of paradise from New Guinea.

Valuable specimens not unfrequently find their way into museums thus managed. Their public-spirited owners fondly imagine that they will be preserved and made of use to the world if once given to such an institution. Their fate is, unfortunately, far otherwise. Dirty, neglected, without label, their identity lost, they are often finally devoured by insects or cleared away to make room on the crowded shelves for the new donation of some fresh patron of the institution. It would be far better that such museums should never be founded. They are traps into which precious—sometimes priceless—objects fall only to be destroyed; and what, is still worse, they bring discredit on all similar institutions, make the very name of museum a byword and a reproach, hindering instead of advancing the recognition of their value as agents in the great educational movement of the age.

A museum is like a living organism—it requires continual and tender care, it must grow or it will perish; and the cost and labour required to maintain it in a state of vitality is not yet by any means fully realised or provided for, either in our great national establishments or in our smaller local institutions.

Often as it has been said, it cannot be too often repeated, that the real objects of forming collections, of whatever kind (apart, of course, from the mere pleasure of acquisition—sometimes the only motive of private collectors), and which, although in very different degrees, and often without being recognised, underlie the organisation of all museums, are two, which are quite distinct, and sometimes even conflicting. The first is to advance or increase the knowledge of some given subject. This is generally the motive of the individual collector, whose experience shows him the vast assistance in forming definite ideas in any line of research in which he may be occupied that may be derived from having the materials for its study at his own command, to hold and to handle, to examine and compare, to take up and lay aside whenever the favourable moment to do so occurs. But unless his subject is a very limited one, or his means the reverse, he soon finds the necessity of consulting collections based on a larger scale than his own. Very few people have any idea of the multiplicity of specimens required for the purpose of working out many of the simplest problems concerning the life-history of animals or plants. The naturalist has frequently to ransack all the museums, both public and private, of Europe and America in the endeavour to compose a monograph of a single common genus, or even species, that shall include all questions of its variation, changes in different seasons, and under different climates and conditions of existence, and the distribution in space and time of all its modifications. He often has to confess at the end that he has been baffled in his research for want of the requisite materials for such an undertaking. Of course this ought not to be, and the time will come when it will not be, but that time is very far off yet.

We all know the old saying that the craving for riches grows as the wealth itself increases. Something similar is true of scientific collections brought together for the purpose of advancing knowledge. The larger they are the more their deficiencies seem to become conspicuous; the more desirous we are to fill up the gaps which provokingly interfere with our extracting from them the complete story they have to tell.

Such collections are, however, only for the advanced student, the man who has already become acquainted with the elements of his science, and is in a position, by his knowledge, by his training, and by his observing and reasoning capacity, to take advantage of such material to carry on the subject to a point beyond that at which he takes it up.

But there is another and a far larger class to whom museums are or should be a powerful means of aid in acquiring knowledge. Among such those who are commencing more serious studies may be included; but I especially refer to the much more numerous class, and one which it may be hoped will year by year bear a greater relative proportion to the general population of the country, who, without having the time, the opportunities, or the abilities to make a profound study of any branch of science, yet take a general interest in its progress, and wish to possess some knowledge of the world around them and of the principal facts ascertained with regard to it, or at least some portions of it. For such persons museums may be, when well organised and arranged, of benefit to a degree that at present can scarcely be realised.

To diffuse knowledge among persons of this class is the second of the two purposes of museums of which I have spoken.

I believe that the main cause of what may be fairly termed the failure of the majority of museums—especially museums of natural history—to perform the functions that might be legitimately expected of them is that they nearly always confound together the two distinct objects which they may fulfil, and by attempting to combine both in the same exhibition practically accomplish neither.

In accordance with which of those two objects, which may be briefly called *research* and *instruction*, is the main end of the museum, so should the whole be primarily arranged; and in accordance with the object for which each specimen is required, so should it be treated.

The specimens kept for research, for advancement of

knowledge, for careful investigations in structure and development, or for showing the minute distinctions which must be studied in working out the problems connected with variations of species according to age, sex, season, or locality; for fixing the limits of geographical distribution, or determining the range in geological time, must be not only exceedingly numerous (so numerous, indeed, that it is almost impossible to put a limit on what may be required for such purposes), but they must also be kept under such conditions so as to admit of ready and close examination and comparison.

If the whole of the specimens really required for enlarging the boundaries of zoological or botanical science were to be displayed in such a manner that each one could be distinctly seen by any visitor sauntering through the public galleries of a museum, the vastness and expense of the institution would be out of all proportion to its utility; the specimens themselves would be quite inaccessible to the examination of all those capable of deriving instruction from them, and, owing to the injurious effects of continued exposure to light upon the greater number of preserved natural objects, would ultimately lose a large part of their permanent value. Collections of this kind must, in fact, be treated as the books in a library, and be used only for consultation and reference by those who are able to read and appreciate their contents. To demand, as has been ignorantly done, that all the specimens belonging to our national museums, for instance, should be displayed in cases in the public galleries, would be equivalent to asking that every book in a library, instead of being shut up and arranged on shelves for consultation when required, should have every single page framed and glazed and hung on the walls, so that the humblest visitor as he passes along the galleries has only to open his eyes and revel in the wealth of literature of all ages and all countries, without so much as applying to a custodian to open a case. Such an arrangement is perfectly conceivable. The idea from some points of view is magnificent, almost sublime. But imagine the space required for such an arrangement of the national library of books, or, indeed, of any of the smallest local libraries; imagine the inconvenience to the real student, the disadvantages which he would be under in reading the pages of any work fixed in an immovable position beneath a glass case; think of the enormous distances he would often have to traverse to compare a reference or verify a quotation, and the idea of sublimity soon gives place to its usual antithesis. The attempt to display every bird, every insect, shell, or plant which is or ought to be in any of our great museums of reference would produce an exactly similar result.

In the arrangement of collections designed for research, which, of course, will contain all those precious specimens called "types," which must be appealed to through all time to determine the species to which a name was originally given, the principal points to be aimed at are—the preservation of the objects from all influences deleterious to them, especially dust, light, and damp; their absolutely correct identification, and record of every circumstance that need be known of their history; their classification and storage in such a manner that each one can be found without difficulty or loss of time; and, both on account of expense as well as convenience of access, they should be made to occupy as small a space as is compatible with these requirements. They should be kept in rooms provided with suitable tables and good light for their examination, and within reach of the necessary books of reference on the particular subjects which the specimens illustrate. Furthermore, the rooms should be so situated that the officers of the museum, without too great hindrance to their own work, can be at hand for occasional assistance and supervision of the student, and if collections of research and exhibited specimens are contained in one building, it is obvious that the closer the contiguity in which those of any particular group are placed the greater will be the convenience both of students and curators, for in very few establishments will it be possible to form each series on such a scale as to be entirely independent of the other.

On the other hand, in a collection arranged for the instruction of the general visitor, the conditions under which the specimens are kept should be totally different. In the first place, their numbers must be strictly limited, according to the nature of the subject to be illustrated and the space available. None must be placed too high or too low for ready examination. There must be no crowding of specimens one behind the other, every one being perfectly and distinctly seen, and with a clear space around it. Imagine a picture gallery with half the pictures on the walls partially or entirely concealed by others hung in front of them; the idea seems preposterous, and yet this is the approved arrangement of specimens in most public museums. If an object is worth putting into a gallery at all it is worth such a position as will enable it to be seen. Every specimen exhibited should be good of its kind, and all available skill and care should be spent upon its preservation and rendering it capable of teaching the lesson it is intended to convey. And here I cannot refrain from saying a word upon the sadly neglected art of taxidermy, which continues to fill the cases of most of our museums with wretched and repulsive caricatures of mammals and birds, out of all natural proportions, shrunken here and bloated there, and in attitudes absolutely impossible for the creature to have assumed while alive. Happily there may be seen occasionally, especially were amateurs of artistic taste and good knowledge of natural history have devoted themselves to the subject, examples enough—and you are fortunate in possessing them in Newcastle—to show that an animal can be converted after death, by a proper application of taxidermy, into a real life-like representation of the original, perfect in form, proportions, and attitude, and almost, if not quite, as valuable for conveying information on these points as the living creature itself. The fact is that taxidermy is an art resembling that of the painter or rather the sculptor; it requires natural genius as well as great cultivation, and it can never be permanently improved until we have abandoned the present conventional low standard and low payment for "bird-stuffing," which is utterly inadequate to induce any man of capacity to devote himself to it as a profession.

To return from this digression, every specimen exhibited should have its definite purpose, and no absolute duplicate should on any account be permitted. Above all, the purpose for which each specimen is exhibited, and the main lesson to be derived from it, must be distinctly indicated by the labels affixed, both as headings of the various divisions of the series, and to the individual specimens. A well-arranged educational museum has been defined as a collection of instructive labels illustrated by well-selected specimens.

What is, or should be, the order of events in arranging a portion of a public museum? Not, certainly, as too often happens now, bringing a number of specimens together almost by haphazard, and cramming them as closely as possible in a case far too small to hold them, and with little reference to their order or to the possibility of their being distinctly seen. First, as I said before, you must have your curator. He must carefully consider the object of the museum, the class and capacities of the persons for whose instruction it is founded, and the space available to carry out this object. He will then divide the subject to be illustrated into groups, and consider their relative proportions, according to which he will plan out the space. Large labels will next be prepared for the principal headings, as the chapters of a book, and smaller ones for the various sub-divisions. Certain propositions to be illustrated, either in the structure, classification, geographical distribution, geological position, habits, or evolution of the subjects dealt with, will be laid down and reduced to definite and concise language. Lastly will

come the illustrative specimens, each of which as procured and prepared will fall into its appropriate place. As it is not always easy to obtain these at the time that they are wanted, gaps will often have to be left, but these, if properly utilised by drawings or labels, may be made nearly as useful as if occupied by the actual specimens.

A public exhibition which is intended to be instructive and interesting must never be crowded. There is, indeed, no reason why it ever should be. Every such exhibition whether on a large or small scale, can only contain a representative series of specimens, selected with a view to the needs of the particular class of persons who are likely to visit the gallery, and the number of specimens exhibited should be adapted to the space available. There is, therefore, rarely any excuse for filling it up in such a manner as to interfere with the full view of every specimen shown. A crowded gallery, except in some very exceptional circumstances, at once condemns the curator, as the remedy is generally in his own hands. In order to avoid it he has nothing to do but sternly to eliminate all the less important specimens. If any of these possess features of historical or scientific interest demanding their permanent preservation, they should be kept in the reserve collections; if otherwise, they should not be kept at all.

The ideal public museums of the future will, however, require far more exhibition space than has hitherto been allowed; for though the number of specimens shown may be fewer than is often thought necessary now, each will require more room if the conditions above described are carried out, and especially if it is thought desirable to show it in such a manner as to enable the visitor to realise something of the wonderful complexity of the adaptations which bring each species into harmonious relation with its surrounding conditions. Artistic reproductions of natural environments, illustrations of protective resemblances, or of special modes of life, all require much room for their display. This method of exhibition, wherever faithfully carried out, is, however, proving both instructive and attractive, and will doubtless be greatly extended.

Guide-books and catalogues are useful adjuncts, as being adapted to convey fuller information than labels, and as they can be taken away for study during the intervals of visits to the museum, but they can never supersede the use of labels. Anyone who is in the habit of visiting picture galleries where the names of the artists and the subject are affixed to the frame, and others in which the information has in each case to be sought by reference to a catalogue, must appreciate the vast superiority in comfort and time-saving of the former plan.

Acting upon such principles as these, every public gallery of a museum, whether the splendid saloon of a national institution or the humble room containing the local collection of a village club, can be made a centre of instruction, and will offer interests and attractions which will be looked for in vain in the majority of such institutions at the present time.

One of the best illustrations of the different treatment of collections intended for research or advancement of knowledge, and for popular instruction or diffusion of knowledge, is now to be seen in Kew Gardens, where the admirably constructed and arranged herbarium answers the first purpose, and the public museums of economic botany the second. A similar distinction is carried out in the collections of systematic botany in the natural history branch of the British Museum, with the additional advantage of close contiguity; indeed, as an example of a scheme of good museum arrangement (although not perfect yet in details) I cannot do better than refer to the upper story of the east wing of that institution. The same principles, little regarded in former times in this country, and still unknown in some of the largest Continental museums, are gradually pervading every department of the institution, which, from its natonal character, its metropolitan position, and exceptional resources, ought to illustrate in perfection the ideal of a natural history museum. In fact, it is only in a national institution that an exhaustive research collection in all branches of natural history, in which the specialist of every group can find his own subject fully illustrated, can or ought to be attempted.

As the actual comparison of specimen with specimen is the basis of zoological and botanical research, and as work done with imperfect materials is necessarily imperfect in itself, it is far the wisest policy to concentrate in a few great central institutions, the number and situation of which must be determined by the population and the resources of the country, all the collections, especially those containing specimens already alluded to as so dear to the systematic naturalist, known as author's "types," required for original investigations. It is far more advantageous to the investigator to go to such a collection and take up his temporary abode there, while his research is being carried out, with all the material required at his hand at once, than to travel from place to place and pick up piecemeal the information he requires, without opportunity of direct comparison of specimens.

I do not say that collections for special study, and even original research, should not, under particular circumstances and limitations, be formed at museums other than central national institutions, or that nothing should be retained in provincial museums but what is of a directly educational or elementary nature. A local collection, illustrating the fauna and flora of the district, should be part of every such museum; and this may be carried to almost any amount of detail, and therefore in many cases it would be very unadvisable to exhibit the whole of it. A selection of the most important objects may be shown under the conditions described above, and the remainder carefully preserved in cabinets for the study of specialists.

It is also very desirable in all museums, in order that the exhibited series should be as little disturbed as possible in arrangement, and be always available for the purpose for which it is intended, that there should be, for the use of teachers and students, a supplementary set of common objects, which, if injured, could be easily replaced. It must not be forgotten that the zealous investigator and the conscientious curator are often the direst antagonists: the one endeavours to get all the knowledge he can out of a specimen, regardless of its ultimate fate, and even if his own eyes alone have the advantage of it; the other is content if a limited portion only is seen, provided that can be seen by everyone both now and hereafter.

Such, then, is the primary principle which ought to underlie the arrangement of all museums—the distinct separation of the two objects for which collections are made; the publicly exhibited collection being never a store-room or magazine, but only such as the ordinary visitor can understand and profit by, and the collection for students being so arranged as to afford every facility for examination and research. The improvements that can be made in detail in both departments are endless, and to enter further into their consideration would lead me far beyond the limits of this address. Happily, as I said before, the subject is receiving much attention.

I would willingly dwell longer upon it—indeed I feel that I have only been able to touch slightly and superficially upon many questions of practical interest, well worthy of more detailed consideration—but time warns me that I must be bringing this discourse to a close, and I have still said nothing in reference to subjects upon which you may expect some words on this occasion. I mean those great problems concerning the laws which regulate the evolution of organic beings, problems which agitate the minds of all biologists of the present day, and the solution of which is watched with keen interest by a far wider circle—a circle, in fact, coincident with the intelligence and education of the world. Several communications connected with these problems will be brought before the sectional meetings during the next few days,

and we shall have the advantage of hearing them discussed by some of those who, by virtue of their special attention to and full knowledge of these subjects, are most competent to speak with authority. It is therefore for me rather delicate ground to tread upon, especially at the close of a discourse mainly devoted to another question. I will, however, briefly point out the nature of the problems and the lines which the endeavour to solve them will probably take, without attempting to anticipate the details which you will doubtless hear most fully and ably stated elsewhere.

I think I may safely premise that few, if any, original workers at any branch of biology appear now to entertain serious doubt about the general truth of the doctrine that all existing forms of life have been derived from other forms by a natural process of descent with modification, and it is generally acknowledged that to the records of the past history of life upon the earth we must look for the actual confirmation of the truth of a doctrine which accords so strongly with all we know of the present history of living beings.

Professor Huxley wrote in 1875:—"The only perfectly safe foundation for the doctrine of evolution lies in the historical, or rather archæological, evidence that particular organisms have arisen by the gradual modification of their predecessors, which is furnished by fossil remains. That evidence is daily increasing in amount and in weight, and it is to be hoped that the comparisons of the actual pedigree of these organisms with the phenomena of their development may furnish some criterion by which the validity of phylogenic conclusions deduced from the facts of embryology alone may be satisfactorily tested."

Palæontology, however, as we all know, reveals her secrets with no open hand. How can we be reminded of this more forcibly than by the discovery announced scarcely three months ago by Professor Marsh of numerous mammalian remains from formations of the Cretaceous period, the absence of which had so long been a source of difficulty to all zoologists? What vistas does this discovery open of future possibilities, and what thorough discredit, if any were needed, does it throw on the value of negative evidence in such matters! Bearing fully in mind the necessary imperfection of the record we have to deal with, I think that no one taking an impartial survey of the recent progress of palæontological discovery can doubt that the evidence in favour of a gradual modification of living forms is still steadily increasing. Any regular progressive series of changes of structure coinciding with changes in time can of course only be expected to be preserved and to come again before our eyes under such a favourable combination of circumstances as must be of most rare occurrence; but the links, more or less perfect, of many such series are continually being revealed, and the discovery of a single intermediate form is often of immense interest as indicating the path along which the modification from one apparently distinct form to another may have taken place.

Though palæontology may be appealed to in support of the conclusion that modifications have taken place as time advanced, it can scarcely afford any help in solving the more difficult problems which still remain as to the methods by which the changes have been brought about.

Ever since the publication of what has been truly described as the "creation of modern natural history," Darwin's work on the "Origin of Species," there has been no little controversy as to how far all the modifications of living forms can be accounted for by the principle of natural selection or preservation of variations best adapted for their surrounding conditions, or whether any, and if so what, other factors have taken part in the process of organic evolution.

It certainly cannot be said that in these later times the controversy has ended. Indeed, those who are acquainted with scientific literature must know that notes struck at the last annual meeting of this Association produced a series of reverberations, the echoes of which have hardly yet died away.

Within the last few months also two important works have appeared in our country, which have placed in an accessible and popular form many of the data upon which the most prevalent views on the subject are based.

The first is "Darwinism: an Exposition of the Theory of Natural Selection, with some of its Applications," by Alfred Russel Wallace. No one could be found so competent to give such an exposition of the theory as one who was, simultaneously with Darwin, its independent originator, but who, by the title he has chosen no less than by the contents of the book, has, with rare modesty and self-abnegation, transferred to his fellow-labourer all the merit of the discovery of what he evidently looks upon as a principle of overwhelming importance in the economy of nature: "supreme," indeed, he says, "to an extent which even Darwin himself hesitated to claim for it."

The other work I refer to is the English translation of the remarkable "Essays upon Heredity and Kindred Biological Problems," by Dr. August Weismann, published at the Oxford Clarendon Press, in which is fully discussed the very important but still open question—a question which was brought into prominence at our meeting at Manchester two years ago—of the transmission or non-transmission to the offspring of characters acquired during the lifetime of the parent.

It is generally recognised that it is one of the main elements of Darwin's, as well as of every other theory of evolution, that there is in every individual organic being an innate tendency to vary from the standard of its predecessors, but that this tendency is usually kept under the sternest control by the opposite tendency to resemble them, a force to which the terms "heredity" and "atavism" are applied. The causes of this initial tendency to vary, as well as those of its limits and prevailing direction, and the circumstances which favour its occasional bursting through the constraining principle of heredity, offer an endless field for speculation. Though several theories of variation have been suggested, I think that no one would venture to say we have passed beyond the threshold of knowledge of the subject at present.

Taking for granted, however, as we all do, that this tendency to individual variation exists, then comes the question, What are the agents by which, when it has asserted itself, it is controlled or directed in such a manner as to produce the permanent or apparently permanent modifications of organic structures which we see around us? Is "survival of the fittest" or preservation by natural selection of those variations best adapted for their surrounding conditions (the essentially Darwinian or still more essentially Wallacian doctrine) the sole or even the chief of these agents? Can isolation, or the revived Lamarckian view of the direct action of the environment, or the effects of use or disuse accumulating through generations, either singly or combined, account for all? or is it necessary to invoke the aid of any of the numerous subsidiary methods of selection which have been suggested as factors in bringing about the great result?

Anyone who has closely followed these discussions, especially those bearing most directly upon what is generally regarded as the most important factor of evolution—natural selection, or "survival of the fittest,"—cannot fail to have noticed the appeal constantly made to the advantage, the utility, or otherwise of special organs or modifications of organs or structures to their possessors. Those who have convinced themselves of the universal application of the doctrince of natural selection hold that every particular structure or modification of structure must be of utility to the animal or plant in which it occurs, or to some ancestor of that animal or plant, otherwise it could not have come into existence; the only reservation being for cases which are explained by the principle which Darwin called "correlation of growth." Thus the extreme natural selectionists and the old-fashioned school of teleologists are so far in agreement.

On the other hand, it is held by some that numerous structures and modifications of structures are met with in nature which are manifestly useless; it is even confidently stated that there are many which are positively injurious to their possessor, and therefore could not possibly have resulted from the action of natural selection of favourable variations. Organs or modifications when in an incipient condition are especially quoted as bearing upon this difficulty. But here, it seems to me, we are continually appealing to a criterion by which to test our theories of which we know far too little, and this (though often relied upon as the strongest) is, in reality, the weakest point of the whole discussion.

Of the variations of the form and structure of organic bodies we are beginning to know something. Our museums, when more complete and better organised, will teach us much on this branch of the subject. They will show us the infinite and wonderful and apparently capricious modifications of form, colour, and of texture to which every most minute portion of the organisation of the innumerable creatures which people the earth is subject. They will show us examples of marvellously complicated and delicate arrangements of organs and tissues in many of what we consider as almost the lowest and most imperfectly organised groups of beings with which we are acquainted. But as to the use of all these structures and modifications in the economy of the creatures that possess them, we know, I may almost say, nothing, and our museums will never teach us these things. If time permitted I might give numerous examples in the most familiar of all animals, whose habits and actions are matters of daily observation, with whose life-history we are as well acquainted almost as we are of our own, of structures the purposes of which are still most doubtful. There are many such even in the composition of our own bodies. How, then, can we expect to answer such questions when they relate to animals known to us only by dead specimens, or by the most transient glimpses of the living in a state of nature, or when kept under the most unnatural conditions in confinement? And yet this is actually the state of our knowledge of the vast majority of the myriads of living beings which inhabit the earth. How can we, with our limited powers of observation and limited capacity of imagination, venture to pronounce an opinion as to the fitness or unfitness for its complex surroundings of some peculiar modification of structure found in some strange animal dredged up from the abysses of the ocean, or which passes its life in the dim seclusion of some tropical forest, and into the essential conditions of whose existence we have at present no possible means of putting ourselves in any sort of relation?

How true it is that, as Sir John Lubbock says, "we find in animals complex organs of sense richly supplied with nerves, but the functions of which we are as yet powerless to explain. There may be fifty other senses as different from ours as sound is from sight; and even within the boundaries of our own senses there may be endless sounds which we cannot hear, and colours as different as red from green of which we have no conception. These and a thousand other questions remain for solution. The familiar world which surrounds us may be a totally different place to other animals. To them it may be full of music which we cannot hear, of colour which we cannot see, of sensations which we cannot conceive."

The fact is that nearly all attempts to assign purposes to the varied structures of animals are the merest guesses and assumptions. The writers on natural history of the early part of the present century, who "for every why must have a wherefore," abound in these guesses, which wider knowledge shows to be untenable. Many of the arguments for or against natural selection, based upon the assumed utility or equally assumed uselessness of animal and vegetable structures, have nothing more to recommend them. In fact, to say that any part of the organisation of an animal or plant, or any habit or instinct with which it is endowed, is useless, or even injurious, seems to me an assumption which, in our present state of knowledge, we are not warranted in making. The time may come when we shall have more light, but infinite patience and infinite labour are required before we shall be in a position to speak dogmatically on these mysteries of nature—labour not only in museums, laboratories, and dissecting-rooms, but in the homes and haunts of the animals themselves, watching and noting their ways amid their natural surroundings, by which means alone we can endeavour to penetrate the secrets of their life-history. But until that time comes, though we may not be quite tempted to echo the despairing cry of the poet, "Behold, we know not anything," a frank confession of ignorance is the most straightforward, indeed the only honest position we can assume when questioned on these subjects.

However much we may be convinced of the supreme value of scientific methods of observation and of reasoning, both as mental training of the individual and in the elucidation of truth and advancement of knowledge generally, it is impossible to be blind to the fact that we, who are engaged with the investigation of those subjects which are commonly accepted as belonging to the domain of physical science, are unfortunately not always, by virtue of being so occupied, possessed of that most precious gift, "a right judgment in all things."

No one intimately acquainted with the laborious and wavering steps of scientific progress (I can answer at least for one branch of it) can look upon that progress with a perfect feeling of satisfaction.

Can it be said of any of us that our observations are always accurate, the materials on which they are based always sufficient, our reasoning always sound, our conclusions always legitimate? Is there any subject, however limited, of which our knowledge can be said to have reached finality? Or if it happens to any of us as to—

> A man who looks at glass
> On it may stay his eye,
> Or if he pleases through it pass
> And then the heavens espy,

are not those heavens which are beyond the immmediate objects of our observation coloured by our prejudies, prepossessions, emotions, or imagination, as often as they are defined by any profound insight into the depth of nature's laws? In most of these questions an open mind and a suspended judgment appear to me the true scientific position, whichever way our inclinations may lead us.

For myself, I must own that when I endeavour to look beyond the glass, and frame some idea of the plan upon which all the diversity in the organic world has been brought about, I see the strongest grounds for the belief, difficult as it sometimes is in the face of the strange, incomprehensible, apparent defects in structure, and the far stranger, weird, ruthless savagery of habit, often brought to light by the study of the ways of living creatures, that natural selection, or survival of the fittest, has, among other agencies, played a most important part in the production of the present condition of the organic world, and that it is a universally acting and beneficent force continually tending towards the perfection of the individual, of the race, and of the whole living world.

I can even go further and allow my dream still thus to run—

> Oh yet we trust that somehow good
> Will be the final goal of ill,—
>
> That nothing walks with aimless feet,
> That not one life shall be destroyed
> Or cast as rubbish to the void
> When God hath made the pile complete.

A Cause of Error in Detecting and Determining Albumen.—C. Patein.—After determining albumen by heat and acetic acid it is necessary to ascertain if the filtrate does not yield a further precipitate with nitric acid.—*Comptes Rendus*, Vol. cix., No. 7.

THE LUNDBERG CASE.†

By ELWYN WALLER, Ph.D.

(Concluded from p. 119).

Resumé of Results on Phosphorus.

Number of Analysts:—15.

Number of Determinations:—NB GPH, 65; SBVE, 34; NB^B BK, 35.

Maximum Variations of Different Analysts upon the Same Pigs:—

NB GPH, 0·0419 (A. H. Sherrerd) to 0·053 (J. M. Sherrerd). Diff. = 0·0111.

SBVE 0·0336 (T. M. Drown) to 0·044 (A. S. Bertolet). Diff. = 0·0104.

NB^B BK, 0·0405 (T. M. Drown) to 0·050 (A. S. Bertolet). Diff. = 0·0095.

Maximum Variations in the Same Brand:—

NB GPH, 0·02 [sample *a* (S. B. Sharples)] to 0·0544 [sample *f* (J. M. Sherrerd)]. Diff. = 0·0344.

SBVE, 0·033 [sample *d* (E. B. Hills)] to 0·0424 [sample *g* (J. M. Sherrerd)]. Diff. = 0·0094.

NB^B BK, 0·0402 [sample *k* (A. S. McCreath)] to 0·050 [sample *b* (A. S. Bertolet)]. Diff. = 0·0098.

Results for Sulphur.

As the case was made to turn chiefly on the percentage of phosphorus present in the iron, many of the analysts made no examination for either sulphur or silicon.

Sharples appears to have followed essentially the same method.

Mr. Elliott precipitated the iron with ammonia in the solution filtered from the silica, and in the filtrate from the iron added barium chloride after acidulating.

The evolution method used by Messrs. Drown, Shimer, and A. H. Sherrerd is the one sometimes known as "Drown's method for sulphur." It consists in treating the iron in a flask with hydrochloric acid, and passing the gases evolved through potassium permanganate solution; after destroying the excess of permanganate by heating with hydrochloric acid the sulphur was precipitated with barium chloride. Messrs. Drown and Shimer testified to treating the residue in the evolution-flask with aqua regia to recover any sulphur that might have been retained.

Dr. Wuth used the same mode of expelling the sulphur from its combination with the iron, but previously filled the evolution-flask with hydrogen, and the evolved gases were by him passed through an alkaline solution of lead. The precipitate, consisting chiefly of lead sulphide, was fused with alkaline carbonate and nitrate, and in the solution from this fusion, after evaporation to dryness with hydrochloric acid, the barium precipitation was conducted as usual.

Resumé of Results on Sulphur.

Number of Analysts:—11.

Number of Determinations:—NB GPH, 12; SBVE, 15; NB^B BK, 12.

Sulphur.

Analyst.	Sample.	Grms. taken.	Method of Analysis.	Furnace Marks. NB GPH.	SBVE.	NB^B BK.
S. B. Sharples	*a*	—	A Dir.	trace	trace	trace
A. H. Elliott	*c*	5	Cl filtr.	none	none	none
E. B. Hills	*d*	—	—	none	none	none
J. M. Sherrerd	*e*	—	—	—	0·011	—
P. W. Shimer	„	7	Ev. Mn.	—	0·019, 0·013	—
A. S. Bertolet	*f*	—	—	0·038	—	—
A. M. Sherrerd	*l*	5	Ev. Mn.	0·3005	0·0008	0·00067
T. M. Drown	„	5—6	Ev. Mn.	0·024	0·033	0·019
S. A. Ford	„	4—5	A Dir.	0·0085, 0·0052	0·0102, 0·0075	0·0167, 0·0166
W. O. Wuth	„	10	Ev. Pb.	0·018	0·020	0·023
T. H. Garrett	„	—	—	trace	0·007, 0·005	0·011, 0·007
A. S. Bertolet	„	—	—	0·039	0·027	0·023
J. M. Sherrerd	„	—	—	0·0074	—	0·011

In the table of results, under methods of analysis, the letters A, N, and Cl have the same significance as to the solvents used as in the phosphorus table. *Dir.* signifies that the precipitation of the barium sulphate was effected in presence of all the iron after solution. *Ev.*, that the sulphur was set free from the sample by treatment. *Filtr.*, that the iron in this solution was precipitated out by ammonia, and the sulphur determined in the filtrate with HCl in a suitable apparatus. *Mn*, that the gas thus evolved was passed through a solution of potassium permanganate (Drown, *Am. Chem. Journ.*, iv., 423). *Pb*, that it was passed through a solution of lead salt.

Methods used for the Determination of Sulphur.

The "direct" method used by Mr. Ford was described by him as having been performed thus:—The iron was dissolved in nitric acid with addition of a little hydrochloric; after effecting solution more hydrochloric acid was added, and the solution evaporated to dryness and heated, the mass taken up with hydrochloric acid, and the solution evaporated until ferric chloride began to crystallise out. It was then diluted, filtered, barium chloride solution added, and the mixture allowed to stand (warm) over night, then filtered, &c., as usual. Mr.

† From the *School of Mines Quarterly*, Vol. x., No. 3, April, 1889.

Maximum Variations of Different Analysts on the Same Pigs:—

NB GPH, trace (T. H. Garrett) to 0·039 (A. S. Bertolet) Diff. = 0·039.

SBVE, 0·0008 (A. M. Sherrerd) to 0·033 (T. M. Drown). Diff. = 0·0322.

NB^B BK, 0·00067 (A. M. Sherrerd) to 0·023 (W. O Wuth and A. S. Bertolet). Diff. = 0·02233.

Maximum Variations in the Same Brand:—

NB GPH, none [sample *c* (A. H. Elliott) and *d* (E. B. Hills)] to 0·039 [sample *l* (A. S. Bertolet)].

SBVE none [samples *c* (A. H. Elliott) and *d* (E. B. Hills) to 0·033 [sample *l* (T. M. Drown)].

NB^B BK none [samples *c* (A. H. Elliott) and *d* (E. B. Hills)] to 0·023 [sample *l* (Wuth and Bertolet)].

Results for Silicon.

In the table as before, under "methods of analysis," the first letters are intended to suggest the solvent used. The other abbreviations used will be explained in the fuller descriptions of the methods.

Messrs. Drown, A. M. Sherrard, and Shimer used the method known as Drown's,* which consists in beginning

* *Trans. Am. Inst. Min. Eng.*, vii., 346.

Silicon.

Analyst.	Sample.	Grms. taken.	Method of Analysis.	Furnace Marks. NB GPH.	SBVE.	NB^B BK.
S. B. Sharples.. ..	*a*	—	A	0·72	1·05	0·69
A. H. Elliott	*c*	5	Cl +	0·979, 0·971	1·113	1·192
E. B. Hills	*d*	—	—	0·96	0·9	0·95
J. M. Sherrerd.. ..	*e*	—	—	—	0·87	—
P. W. Shimer	,,	1	N Drown.	—	0·841, 0·822	—
A. S. Bertolet	*f*	—	—	0·813	—	—
J. M. Sherrerd.. ..	,,	—	—	0·961	—	—
A. M. Sherrerd ..	*l*	5?	N Drown.	1·106, 1·120	0·812, 0·812	1·26, 1·26
T. M. Drown	,,	1—1·5	N Drown.	1·112, 1·152	0·838, 0·832	1·237, 1·234
S. A. Ford	,,	2—3	HCl loss KHO	1·065, 1·061	0·801, 0·781	1·190, 1·190
T. H. Garrett	,,	3—4	N loss HF +	1·116, 1·107	0·822, 0·821	1·239, 1·232
A. S. Bertolet	,,	—	—	1·058	0·769	1·177
J. M. Sherrerd.. ..	,,	—	—	1·078	—	1·195
W. O. Wuth	,,	2	N HCl fus.	1·05	0·77	1·190

solution with nitric acid, then adding sulphuric in sufficient excess, and dehydrating the silica by evaporating down to concentrated sulphuric acid. Mr. Elliott ignited and weighed the residue obtained by evaporation of the solution of the portion taken for phosphorus. The + sign in the table signifies that that portion of the sample was used for some other determination. Dr. Wuth purified the residue left by evaporation of the first acid solution of the iron by fusion with alkaline carbonate, solution in hydrochloric acid, and re-evaporation. Messrs. Garrett and Ford determined the silica by loss, Mr. Garrett taking the residue left by evaporation of the portion taken for phosphorus, and, after ignition and weighing, expelling by means of hydrofluoric acid. On the other hand, Mr. Ford took a separate portion, dissolved in hydrochloric acid (Gr. 1·06), evaporated to dryness, weighed the residue, boiled it with KOH solution (Gr. 1·25), diluted with an equal bulk of water, and again filtered and weighed.

Resumé of Results on Silicon.

Number of Analysts :—11.

Number of Determinations :—NB GPH, 17; SBVE, 16; NB^B BK, 14.

Maximum Variations of Different Analysts on the Same Pigs :—

NB GPH, 0·813 (A. S. Bertolet) to 0·961 (J. M. Sherrerd). Diff. = 0·148.

SBVE, 0·769 (A. S. Bertolet) to 0·838 (T. M. Drown). Diff. = 0·069.

NB^B BK, 1·177 (A. S. Bertolet) to 1·26 (A. M. Sherrerd). Diff. = 0·083.

Maximum Variations in the Same Brand :—

NB GPH, 0·72 [sample *a* (S. P. Sharples)] to 1·152 [sample *l* (T. M. Drown)]. Diff. = 0·432.

SBVE, 0·769 [sample *l* (A. S. Bertolet)] to 1·113 [sample *c* (A. H. Elliott)]. Diff. = 0·344.

NB^B BK, 0·69 [sample *a* (S. P. Sharples)] to 1·26 [sample *l* (A. M. Sherrerd)]. Diff. = 0·570.

Conclusions.

A fair conclusion from these results would seem to be that, as regards *phosphorus*, different analysts having portions of the same pig-iron may obtain results differing from one another by about 0·01 per cent, also that in the same brand of iron about the same difference in phosphorus is to be expected.

As regards *sulphur*, when small in amount the differences to be expected between different analysts on portions of the same pig, or between different samples of the same brand, are comparatively great and very irregular, and hence we must conclude either that sulphur is very irregularly distributed through the iron, or that our present methods of determining that element in manufactured irons need careful revision. Probably both aspects of the case require attention.

As regards *silicon*, portions of the same pig in different hands may show results differing from one another by 0·1 per cent or over; in the same brand the differences may be in the neighbourhood of 0·5 per cent.

As to methods of analysis, there seems to be no good reason for giving a preference to one over any of the others used by the different analysts. In many cases results agreeing closely were obtained on the same sample by different methods, and further, where the same analyst tried the effect of different methods, his results were essentially the same.

CLARKE'S SOAP TEST: PREPARTION OF THE STANDARD SOLUTION.

By F. E. NELSON.

It has long been recognised among chemists that Clarke's soap test, as a measure of the hardness of natural waters, is of only limited application and value.

Mr. A. H. Allen, in a recent paper (*Journ. Soc. Chem. Ind.*, Dec., 1888), has critically discussed, and clearly shown, the defects of the test, at the same time substituting a method of examination of evident superiority; nevertheless, the soap test will not be banished from the laboratory, and I venture to make a suggestion of a very simple method of preparing a standard soap solution of constant composition, which will be sufficiently explained by the following example:—

One grm. of pure palmitic acid was dissolved in a small volume of pure spirit, and neutralised with 4 c.c. normal soda solution (calc. equiv., 3·9 c.c.). This volume of soda solution is equivalent to 4×50 m.grms. $CaCO_3$, and was therefore diluted to 200 c.c., adding so much aqueous spirit that the percentage of alcohol in the standard solution amounted to 35.

This solution I found to give constant results, which, with waters containing only calcium carbonate, are closely approximate to the contents of $CaCO_3$, as determined by titration.

Instead of a pure palmitic acid, fat acids separated from ordinary tallow may be used, neutralising in presence of phenol-phthalein, as indicator, and diluting in accordance with the number of c.c. of normal alkali used.

Laboratory of Messrs. Cross and Bevan,
4, New Court, London, W.C.,
Sept. 3, 1889.

The Presence of Living Germs in Preserved Foods.—MM. Poincarré and Macé.—The authors have detected bacteria in the following "tinned" meats:—Salt beef, ragout of hare, ox tongues, partridge, larks, sardines, salmon, and tunny, and in two vegetables, kidney beans and spinach.—*Journ. de Pharm. et de Chim.*, xix., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 7, August 12, 1889.

The Production of Crystalline Cobaltous and Ferrous Hydrates.—A. de Schulten.—The cobaltous compound is prepared by heating a solution of 10 grms. cobaltous chloride in 60 c.c. water with 250 grms. caustic potassa in a flask of Bohemian glass into which is passed a current of coal-gas. As the temperature rises the cobaltous chloride dissolves in the potassa, which turns to a deep blue. The solution is let settle for twenty-four hours, keeping the flask full of coal-gas. Cobaltous hydrate appears to the naked eye as a deep violet powder, which, under the microscope, appears in quadrangular prismatic crystals. Ferrous hydrate is obtained in a corresponding manner, using soda instead of potassa. Nickel hydroxide is perfectly insoluble in the strongest solutions of potassa and soda.

Journal de Pharmacie et de Chimie. Series 5, Vol. xix., No. 11.

Use of Potassium Permanganate to Detect the Impurities of Alcohol.—P. Cazeneuve.—Already noticed.

Comparative Study of Products obtained by the Fermentation of Amylaceous Matters by Means of Various Kinds of Ferments.—M. Martinand.—Already noticed.

Conversion of Nitro-camphor into Nitroso-camphor.—P. Cazeneuve.—Already noticed.

Analysis of Cinchonas and the Relative Solubility of the Proximate Principles which they Contain in Water, Alcohol, and Dilute Hydrochloric Acid.—E. Landrin.—Already noticed.

Toxicological Search for Mercuric Chloride.—Prof. Ludwig.—The suspected organs are first boiled for several hours with nitric acid. When the mass is completely reduced to a pulp it is placed in a flask (connected to a refrigerator) filled with hydrochloric acid of mean concentration and heated for three or four hours, taking care to stir well. It is then let cool slightly and the liquid is decomposed by means of a small quantity of potassium chlorate; the mixture is filtered to separate the insoluble precipitate and zinc-powder is added. It is stirred for a minute, let settle, and heated again to 50° or 60°, taking care to stir well in order to obtain a complete settlement of the mercury. After letting settle for a day, a small quantity of zinc-powder is again added and the whole process is repeated. The solution is decanted afresh, the collected precipitates are filtered through a funnel stoppered with asbestos, washed, and dried in a current of air. To separate the mercury from the zinc amalgam the author makes use of a tube bent in U-shape at one end, into which there is introduced first a little asbestos, then a layer of lime, then a layer of copper-oxide, and finally the zinc-amalgam. The curved part of the tube which issues out of the furnace is kept cool by means of water. The lime is first heated to redness, then the copper, and lastly the amalgam. A current of air is continually passed through the tube. The mercury separates in drops in the refrigerated part of the apparatus. In this manner, from 97·5 to 98 per cent of the mercury is recovered. Mercury is localised in certain special organs, especially the liver, the spleen, and the kidneys.

Part Played by Alum in Bread-making.—M. Bruylants (see *Journal de Pharmacie*, vol. xix., p. 421).—Alum owes its power of blanching the paste of bread no to the alumina which it contains or to the combination o this earth with the gluten, but to the sulphuric acid liberated by the formation of aluminium albuminate. According to Nothnagel and Rossbach the prolonged daily use of alum in the proportion of 0·05 to 0·1 grm. occasions gastric disturbances not unimportant. The author finds that the artificial gastric digestion of alumed bread effects the solution of all the alum present. Hence it is possible that a quantity of alumina equivalent to 0·20 grm. of alum may enter the circulation daily.

Journal fur Praktische Chemie. Vol. xxxix., Nos. 10 and 11, 1889.

On Pentamethylene and Tetramethylene Bromides.—G. Gustavson and N. Demjanoff.—The boiling-point of pentamethylene is between 204° and 206°, much higher than the boiling-points of all the known amylene bromides. The boiling-point of tetramethylene is between 188° and 190°.

Remarks on a Memoir by Hanriot and Bouveault.—E. von Meyer.—The author shows that he had ascertained the composition and the constitution of the compounds $C_6H_9NaN_2$ and $C_6H_{10}N_2$ four months prior to MM. Hanriot and Bouveault.

MISCELLANEOUS.

Determination of Copper and Arsenic in Pyrites.—R. Nahnsen (*Chemiker Zeitung*).—For determination of copper 12·5 grms. of the dry finely pulverised sample are placed in a beaker of thin glass 17 centimetres in height, and covered with 10 c.c. water and 1 c.c. strong sulphuric acid. Keeping the glass covered with a porcelain capsule, nitric acid of sp. gr. 1·4 is gradually added until effervescence no longer occurs. The liquid is let boil over a moderately strong flame, the porcelain capsule is removed, and the liquid is boiled, whilst being frequently shaken round and round until it becomes tough and scarcely yields to shaking, and yellow saline particles begin to separate out. The paste is then quickly brought into solution by means of warm water, which should be kept ready at hand. The cold solution is transferred to a 250 c.c. flask, filled up, and filtered through a dry filter. 200 c.c. (=10 grms. pyrites) of the solution thus freed from silica and lead are treated for some hours with a brisk current of sulphuretted hydrogen until the precipitate clots together and the liquid appears transparent. It is filtered and washed with pure water, whilst being frequently crushed with a glass rod. Sulphuretted hydrogen water is here unnecessary if the sulphuretted hydrogen has been allowed to act until the liquid appears quite clear. The portion of the precipitate on the filter is rinsed back with a minimum of hot water to the main mass, and so much strong solution of sodium sulphide is added that the liquid, after being heated to a boil for a few minutes, shows no undissolved sulphur. It is diluted with hot water, let stand in a warm place until clear; the solution which contains the arsenic and antimony, and is quite free from copper, is filtered off, and the deposit of copper sulpide is washed with hot water. Traces of iron sulphide which still adhere to the copper sulphide are removed by hot water to which a few drops of hydrochloric acid have been added, the residue is washed until free from chlorine, and the copper determined as sulphide. The copper sulphide is tested for the presence of cadmium or bismuth by dissolving it in nitric acid and treating the solution for some time with ammonium carbonate in heat. The precipitate formed is weighed as oxide and deducted. For determining the arsenic the dissolved sulphuretted hydrogen is expelled from the 200 c.c. of solution by a current of carbonic acid, and arsenic sulphide is extracted from the washed precipitate by means of ammonia. The further treatment may be conducted volumetrically (Leroy W. McCay, Chemical News, xlviii., 7) or gravimetrically (B. Fischer, *Chemiker Zeitung*, ix., 1613).

The Chemical Laboratory of Wiesbaden always enjoys a very large attendance. For the summer term, 1889, there were 68 students on the books; 54 of these worked only in the chemical laboratory, 10 in the bacteriological department, and 4 in both departments. 44 were from Germany, 6 from England, Ireland, and Scotland, 4 from North America, 3 from Holland, 3 from Russia, 2 from Italy, 1 from Luxemburgh, 1 from France, 1 from Spain, 1 from Norway, 1 from Chili, and 1 from Australia. The assistants in the instruction laboratory are 2 in number, in the private laboratory 15, and in the versuchsstation 3. At the end of the summer term, 1889, Dr. med. F. Hueppe left the laboratory because he has been appointed Professor of hygiene at the German University in Prague. His successor is Dr. med. G. Frank, late assistant of Professor von Pettenkofer in Munich, and of Professor Rob. Koch in Berlin. The other teachers are the same as hitherto. The winter term begins on the 15th of October. Besides the scientific researches, a great number of analyses were undertaken in the different departments of the laboratory and the versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

Brewing.—Can any of your readers recommend me a good and not too voluminous work upon the chemistry of brewing?—K.

Tests for Alum.—Could any of your readers give me a few simple tests for alum, either soda or potash? I have been unable to find tests given in any works on the subject.—A Tyro.

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NEW SOUTH WALES.

THE GOVERNMENT OF NEW SOUTH WALES intend to establish METALLURGICAL WORKS on a scale sufficiently large for determining, in bulk, the best methods of treating Ores produced in the Colony.

A SUPERINTENDENT is REQUIRED to erect, control, and direct these Works. He must possess the highest qualifications and widest experience, and it will be his duty to introduce the best methods of treating Ores (especially Auriferous and Argentiferous), with a view to extract therefrom the metals and other substances possessing an economic value. He would also have to impart full instruction in the various methods of treatment, and to afford every facility to Smelters and Miners for acquiring a practical knowledge of the processes employed.

Applications, stating Candidate's age, salary required, and accompanied by copies of testimonials, must be sent, on or before the 25th September, 1889, to The Agent-General for New South Wales, 5, Westminster Chambers, London, S.W.

SAUL SAMUEL,

7th August, 1889. Agent-General for New South Wales.

CHEMICAL LABORATORY,
WIESBADEN, GERMANY.

Director—Prof. R. FRESENIUS, Ph.D.

Practical Instruction in the Laboratory .. .. Prof. R. FRESENIUS, Ph.D. / Prof. H. FRESENIUS, Ph.D. / W. FRESENIUS, Ph.D. / E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D
Experimental Physics .. .. / Stöchiometry .. .. — W. FRESENIUS, Ph.D.
Organic Chemistry .. .. — E. HINTZ, Ph.D.
Chemical Technology .. .. / Microscopy, with exercises in Microscopic work .. .. — E. BORGMANN, Ph.D.
Chemistry and Analysis of Foods .. — Prof. H. FRESENIUS, Ph.D. / E. BORGMANN, Ph.D. / W. FRESENIUS, Ph.D., and / E. HINTZ, Ph.D.
Hygiene .. .. / Practical exercises in Bacteriology .. — Dr. med. G. FRANK.
Technical Drawing, with exercises .. — J. BRAHM.

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. Kreidel's Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

THE LONDON HOSPITAL MEDICAL COLLEGE.

The WINTER SESSION will COMMENCE on TUESDAY, October 1st.

The Hospital, which is the largest general Hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin, and teeth, and for cancer, tumours, diseases of the bladder, piles and fistula. Number of in-patients last year, 8873; out-patients, 101,548; accidents, 7456.

Surgical operations daily.

Appointments:—Resident accoucheur, house physicians, house surgeons. Forty of these appointments are made annually. Numerous dressers, clinical clerks, post-mortem clerks, and maternity assistants are appointed every three months. All appointments are free. Holders of resident appointments are also provided free board. The New College Buildings are now complete, and afford more than double the former accomodation.

Two Entrance Science Scholarships, value £60 and £40, and two Buxton Scholarships, value £30 and £20, will be offered for competition at the end of September to new Students. Sixteen other Scholarships and Prizes are given annually.

Luncheons or dinners at moderate charges can be obtained in the Students' Club.

The London Hospital is now in direct communication with all parts of the Metropolis. The Metropolitan, District, and other Railways have stations within a minute's walk of the Hospital and College.

For further information apply personally, or by letter, to

Mile End, E. MUNRO SCOTT, Warden.

Prof. A. E. FOOTE,

of Philadelphia, Pa.,

Who has the

LARGEST STOCK OF MINERALS AND CHEMICAL AND OTHER SCIENTIFIC BOOKS IN THE WORLD,

Has, for the convenience of his European Customers, established a Branch at

14, RUE DESAIX, PARIS, FRANCE.

This is near Porte Desaix (G), near the Avenue Suffrin, and is less than five minutes' walk from his Exhibit in the Exposition. An Attendant will accompany anyone from the Exhibit to the Store and provide them with a return ticket to the Exposition.

Prof. FOOTE has brought to Paris twelve tons of choice crystallised Minerals, including such beautiful minerals as Red and Yellow Wulfenites, Red, Yellow, and Brown Vanadinites, Colemanite, Azurite, &c. Also such rare species as Colemanite, Gadolinite, Hanksite, Beryllionite, Thenardite, Trona, Borax, &c., &c.

Prof. FOOTE will be glad to meet his English customers at No. 14, Rue Desaix, or to fill orders by express.

THE CHEMICAL NEWS.

Vol. LX. No. 1556.

HINTS TO STUDENTS.

We have in former years repeatedly endeavoured to throw some light upon the important questions, What and in what manner young men should study? To-day we are driven to consider the still more fundamental subjects, Under what circumstances they should study, and even if they should study chemistry at all? Such doubts may, perhaps, seem strangely heretical in face of the general outcry for higher instruction as a cure for the difficulty of earning a livelihood experienced by so many. But they will be found, we submit, more than justified by the present position of affairs both in Britain and elsewhere. Time was, if we may believe an ancient proverb, when "learning was better than house or land." Cultivated intelligence was rare, and, except spoiled by co-existence with dishonesty or idleness, it could almost name its own terms. But in our days the supply has outrun the demand. According to a recent investigation made at Gœttingen the number of young men studying in the different faculties of the German Universities outnumber more than two-fold the possible number of openings when their careers are completed. With us it is no better. We have heard authentic cases of University graduates and even fully qualified physicians and barristers seeking employment as railway-porters. The old learned professions, divinity, law, and medicine, being thus overcrowded, how is it with the no less learned professions of more recent date? The consulting chemist and the engineer, whether he belong to the civil, mechanical, mining, or electrical department—in the last probably less than in the others—are fast reaching, if they have not already reached, the same unenviable position. We see legally qualified medical men announcing that they give advice and medicine for sixpence, and the sums for which scientific chemists undertake to analyse all manner of substances, natural or artificial, can certainly not pay for pure reagents, leaving time out of the question. A correspondent of the Chemical News, "M.A., F.C.S., and F.I.C.," tells us what he was offered for some analytical work. The parties required about 36 samples weekly to be analysed for total solids and butter-fat during the whole season from April to November. For this entire work the parties concerned had previously paid £20, or something less than 4d. per sample! This unpleasant fact stands by no means singly, and we hence submit that any young man will do well to reflect maturely before he spends considerable sums of money and some of the most important years of his life in qualifying himself for the profession of an analytical and consulting chemist.

Now we are often told, and that not without a certain share of truth, that it is merely mediocrity which is crowded, there being "always room enough at the top." The difficulty is, however, that the process of sorting out men of ability from the mass is often very tedious, and, where honours and positions are awarded on the examination system, altogether fallacious.

It must not, however, be supposed that we are seeking to dissuade the young from the study of chemistry altogether. To three classes, who we would fain hope are becoming more numerous, we must recommend it most strongly. In the first place, to all who aim at reaching something higher than a mere Board-school grade of mental culture we should recommend it, quite irrespective of possible material benefits, as a means of intellectual training. Chemistry teaches us the important arts of close and accurate observation, and of drawing correct inferences from the facts recognised. These important arts can never be mastered by the most prolonged study of classics and mathematics. Hence, if we regard education as intellectual discipline, rather than the mere absorption of a number of facts, we shall find some one of the branches of natural and physical science absolutely essential and indispensable. And under most circumstances chemistry will prove the most appropriate subject.

Another class which we should like to see largely recruited consists of men in independent circumstances who have the leisure needed for taking in hand those many scientific problems which are often neglected because they are not immediately remunerative. Such men too commonly waste their time in dissipation, in the pursuit of more wealth, or in making mischief. Now if they possess the needful ability we had much rather see them at work in the laboratory.

The last class to whom we would especially recommend a thorough study of chemical principles are those who are looking forward to employment in the chemical arts, whether as proprietors, managers, foremen, &c. It is a misfortune when men who occupy such positions depend merely upon rule of thumb and traditional recipes.

If these three classes do what we believe is their duty our national manufactures and our national habits of thought will alike undergo a needed improvement.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree granted by this University are required to have passed the Matriculation Examination, and all candidates for Matriculation will henceforth be required to comply with the following instructions:—(1) Not less than five weeks before the commencement of the Examination every candidate must apply to the Registrar, by letter, for a Form of Entry, which, together with all particulars respecting the arrangements for the Examination, will be sent to him immediately on receipt of the application. (2). This form, duly filled up, must be returned to the Registrar not less than four weeks before the commencement of the Examination, and with it, in the same cover, must be sent (*a*) the candidate's certificate of age, and (*b*) his fee for the Examination. No candidate's name will be placed on the list of candidates unless his form of entry, certificate of age, and fee shall have been received at the University on or before the fourth Monday before the commencement of the Examination. As soon as possible after the closing of the list, and not previously, each candidate's certificate and fee will be acknowledged, his certificate will be returned, and a Number, by which he is to be designated throughout the Examination, will be assigned to him.

The Fee for this examination is £2.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June. The

Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages :—Greek, French, German, Sanskrit, or Arabic. The English Language, English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Experimental Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds—their chief physical and chemical characters—their preparation—and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments, provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will be held in July, 1890.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

The Fee for this Examination is £10.

Preliminary Scientific (M.B.) Examination.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination, nor unless he have given notice of his intention to the Registrar at least one calendar month before the commencement of the examination.

The Fee for this examination is Five Pounds.

Examination in Subjects relating to Public Health.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass *at the same time* in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

examination in Classics and Mathematics, which may be done in the first or second term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £80 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, M.D. F.R.S., V.P.C.S.

Assistant Lecturer.—Augustus E. Dixon, M.D., F.C.S.

Demonstrators.— William Early, F.I.C., and Emil A. Werner, F.C.S.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The new Lecture Hall provides full accommodation for 300 Students. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year; advanced, second year.
2. *Organic Chemistry.* — General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

On Tuesday and Thursday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated.

Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry —One Month (daily attendance), £4 4s. od.; Three Months (daily attendance), £10 10s. od.; Six Months (daily attendance), £18 18s. od.; Nine Months (daily attendance), £26 5s. od. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms; Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1889-90, are Tuesday, October 1, Wednesday, January 15, and Wednesday, April 16.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

PHOTOGRAPHY.

Lecturer.—J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be

afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.
Assistant Professor.—R. T. Plimpton, Ph.D.
Assistants.—N. Collie, Ph.D., and H. Smith.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Thursday, October 2nd, until Wednesday, December 18th;

Second Term, from Tuesday, January 7th, 1890, till Tuesday, March 25th;

Third Term, for Lectures, from Tuesday, April 15th, till Tuesday, July 1st. Class Examinations occupy about ten days, beginning on Thursday, June 19th.

Students, who having entered in October do not intend to present themselves in all three subjects at the July Preliminary Science Examination, should during the first term confine their attention to Chemistry, and take this subject alone at the January Examination.

Students entering in January should take Physics and Biology at the July Examination, and Chemistry at the succeeding January Examination.

Junior or Matriculation Course.

Tuesday, Thursday, and Saturday, at 10, commencing October 3, 1889, and April 17th, 1890. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms : Inorganic.—The Class meets four times a week : Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fee :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Intermediate Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Monday, Wednesday, and Friday, at 9, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course for those engaged in prosecuting research in Organic Chemistry will be held three times a week during the Second Term. Fee, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Fridays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee :—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees : for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Laboratory and Classes of Technical Chemistry may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1889-90; also the Clothworker's Scholarship of £50.

Applied Chemistry.

Lecturer, Watson Smith, F.I.C., F.C.S.

During the first and second terms Courses of Lectures will be given on the following subjects :—

Chemistry of the Alkali Trade. Tuesday, 5 to 6 p.m. Fee, £2 2s.

Fuel and Gas. Monday, 5 to 6 p.m. Fee, £2 2s.

Coal-tar Products. Thursday and Friday, 5 to 6 p.m. Fee, £3 3s.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

Residence for Students.

Students can obtain residence at University Hall, Gordon Square. Particulars can be obtained at the office of the College.

NORMAL SCHOOL OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.
Assistant Professor.—F. R. Japp, M.A., Ph.D., F.R.S.
Demonstrators.—H. Chapman Jones and A. E. Tutton.
Assistants.—G. S. Newth, F. Guthrie, and J. W. Rodger.

The Normal School of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is affiliated to the Normal School. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Normal School. The instruction in the Normal School is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Normal School, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Normal School of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins about the 4th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidate being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Agriculture	4	10
Astronomical Physics	2	

Mathematics and Mechanical Drawing £3 per term. Geometrical Drawing, £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Normal School of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Science teachers actually engaged in teaching who are registered by the Science and Art Department as qualified to earn payments for teaching Science may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Three courses of evening lectures for working men will be given during the session in Mining, Astronomy, and Botany. The admission to each course of six lectures will be 6d. The numbe of tickets is limited by the size of the lecture theatre.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.).

The College is open to male and female students above the age of sixteen years. The Session commences on Saturday, September 28, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at

examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

New Chemical Laboratories have been recently built in connection with this College and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Demonstrator, David M. Lewis, M.A.

The Session opens October 1st, 1889. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Elementary Physical Chemistry. Fee for the Term, £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s.

Two Courses of Lectures will be given on Agricultural Chemistry. Fee for each Course, 2s.

In November, 1888, the College received a grant of £200 from Parliament for the promotion of Agricultural Education, and a Committee was appointed to frame a complete scheme of Agricultural Instruction for North Wales. Three Dairy Schools in connection with the College have been established in Welshpool, Denbigh, and Bangor, and an Agricultural Department will be opened next session, in which students may receive a complete training in Agricultural Science.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—J. Tudor Cundall.

The Session commences September 30th, and terminates in June, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

The Laboratory Course may be modified to meet the requirements of individual students wishing to obtain a special knowledge in some branch of manufacturing or industrial chemistry. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours, £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Evening Lectures.—A course of Lectures will be given on Elementary Chemistry.

At the entrance examination in September, and the annual examination in June, several scholarships, &c., are awarded. Great importance is attached to special excellence in one subject.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1889-90 will begin on October 9. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. Excursions to some of the mines, manufactories, and chemical works of the neighbourhood are occasionally made. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College. Full information may be obtained of the Secretary.

Day Lectures.

Inorganic Chemistry.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 10 and 11 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it is closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	7½	15	13	10	5
,, Two Terms ..	5½	11	9	7½	4
,, One Term ..	3	6	5	4	2
,, Month	1½	3	2½	2	—

Students may arrange to divide their days of laboratory work into half-days.

Analytical Course.

A Course of Lectures on the Principles of Qualitative Analysis will be given during the First and Second Terms; it is intended to supplement the instruction in Practical Chemistry. All first year's Laboratory Students are expected to attend this Course. The Lectures will be given on Mondays at 10 a.m. Fee, £1 1s. for the two Terms.

Photographic Chemistry.

Instruction will be given in the Photographic Laboratory in Dry-plate Processes, Printing, Enlarging, and in Microscopical Photography, at times to be arranged with those who enter. Fee, £3 3s. for each Term.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

Evening Lectures.

This course will consist of Two Lectures a week during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures.

Fee, 15s. for Two Terms; 10s. for One Term.

Special Courses of Lectures will be given during the First Term on Chemistry as Applied to Soaps and Candles, Mondays, at 8; and during the Second Term on Chemistry as Applied to the Art of Potting, Mondays, at 8.

With the approval of the Council of the Institute of Chemistry students desiring to qualify as Associates may pass through the requisite amount of study at this College, which has also been approved as a centre for the Practical Examination of the Institute.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S.

Assistant Lecturer.—W. W. J. Nicol, M.A., D.Sc., Edin.

Demonstrator.—Thomas Turner, F.C.S.

The Session will be opened on Monday, October 1st, 1889.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays, at 9.30 a.m. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, and Wednesday at 9.30 a.m. Fee, £1 11s. 6d.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once a week. Fee for the session £3 3s.

Laboratory Practice.

The College Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Threee Terms	18 „	12 „

A Course of short demonstrations and exercises will be given by the Professor or one of his Assistants once a week. All first-year Students will be required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.—Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

Chemistry and Dyeing Department.

Professor.—Edmund Knecht, Ph.D., F.I.C.

Demonstrator.—J. R. Appleyard.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session began on September 16th and terminates on July 7th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—A. G. Bloxam, F.C.S., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.C.S.

Assistant Lecturers.—C. H. Bothamley, F.C.S., and Herbert Ingle.

The Session begins October 3, 1889.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First years' Honours Course, Non-metals, Monday, Wednesday, and Friday, at 9.30 a.m.. Fee, £3 13s. 6d.

3. Inorganic Chemistry. — Second years' Honours Course, Metals. Three hours weekly. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday and Thursday at 11.30 p.m] Fee £2 12s. 6d.

5. Theoretical Chemistry.— Advanced Course. Fee, £1 11s. 6d.

6. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.

7. Photographic Manipulation.—A Course of Ten Lessons will be given on Fridays, from 2 to 5, during the Third Term, with special reference to dry plate processes and silver and platinum printing. Fee, £1.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Evening Classes.

A Course of twenty Lectures by Mr. C. H. Bothamley, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 9. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.C.S.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators.—C. A. Kohn, B.Sc., Ph.D., and S. G. Rawson, D.Sc.

Assistants.—H. H. Froysell and A. C. Wilson.

The Session commences October 3rd.

The Classes are arranged to suit the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry.

Course A.—Non-metals.

Course B.—Chemistry of the Metals.

Course C.—Organic Chemistry.

Course D.—Physical Chemistry.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy.

Course F.—Technological Chemistry: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper. Iron. (3) Distillation of Coal, and Tar Industries. (4) Fuel. (5) Chemistry Applied to Sanitation. (6) Technical Gas Analysis. (7) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate. Saturday, 9.30 a.m. to 12.30 p.m. Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special: For the Conjoint Board of Colleges of Physicians and Surgeons. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class. Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

TABLE OF FEES.

Per Week.	One Month.	One Term, Three Months.	Two Terms, Six Months.	Three Terms, One Session.
One day ..	—	£4	£6	£8
Two days ..	—	6	8	10
Three days..	£4	8	10	12
Four days ..	5	9	12	15
Five days ..	—	10	14	18

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

Technological Curriculum.

First Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics and Mechanics. Engineering Drawing and Design (in this or the following year). French or German. Physics.

Second Year.—Chemistry—Courses A and B; Chemical Laboratory two or three days per week, and the Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work. Mathematics (intermediate), German or French.

Third Year.—Chemistry, Lecture Course on Organic Chemistry, C Lecture Course, E, and Chemical Physics, D. Technological Chemistry, Course F. Chemical Laboratory, four or five days per week. Engineering. The Final Examination for the degree of B.Sc. may be taken if the Student is sufficiently diligent.

Fourth Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. By spending three years after passing the Preliminary Examination of Victoria University, an able Student may take the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on (1) Chemistry of the non-Metals; (2) Chemistry of Photography; (3) Fuel.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 per one year, will be awarded in December on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Laboratory is opened for Students from 10 a.m. to to 5 p.m. daily, on Saturdays from 10 to 1 only.

The Prospectus containing full particulars may be obtained from Adam Holden, 48, Church St., Liverpool, price 6d.; or from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Demonstrator—Saville Shaw.

The Session will commence on October 8th, 1888.

Junior Division: First Year Course.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 17th.

Senior Division: Second Year Course.—A Course about ninety Lectures will be given throughout the Session the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Tuesday, October 15th.

Fee, for either Course, five guineas for the Session.

An Advanced Class will be formed for the study of Theoretical Chemistry. Fee, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 22nd. Fee, £1 1s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the four subjects,—Mathematics, Physics, Chemistry, and Geology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

The examination will be held at the College, and will commence on Monday, October 8th.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—C. Schorlemmer, LL.D., F.R.S.

Demonstrators and Assistant Lecturers.—Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc., Ph.D.

Assistant Demonstrators.—A. Harden, Ph.D., and G. Fowler, B.Sc.

The Session begins on October 1, 1889, and ends on June 20, 1890.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 10.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honour Course.—Mondays, Wednesdays, and Fridays, 3.30 p.m., during the two Winter Terms. The Non-Metals.

Second Year Honour Course.—Mondays, Wednesdays, Fridays, 9.30, during the two Winter Terms. The Metals.

Third Year Honour Course.—Tuesdays, 11.30. Physical Chemistry.

Organic Chemistry (*Honours*).—Tuesdays, Thursdays, Saturdays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Thursdays, 10.30, during the Session.

Technological Chemistry.

First Course.—Sulphuric Acid and Soda Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of the Coal Tar Colours.

An ordinary degree of B.Sc. in Chemistry may be taken at the College in either two or three years, according as the student passes the Preliminary Examination on joining the College or whether he takes a year to prepare for that examination. The Degree of B.Sc. with Honours in Chemistry can be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Exhibitions, &c., are available to students.

Certificates in Applied Chemistry.

The complete course of instruction extends over four years, and embraces the following subjects:—

First Year (Preparatory).—Chemistry Lectures, General Course:—Chemical Laboratory, two days per week. Pure Mathematics. Elementary Mechanics. Geology. French or German. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Second Year.—Chemistry Lectures, First year Honour classes. Chemical Laboratory, three days per week. Technological Chemistry Lectures. Elementary Physics or Mineralogy Lectures and Practical Courses. German or French. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Third Year.—Chemistry Lectures, Second year Honour. Organic Chemistry Lectures. Chemical Philosophy. Chemical Laboratory, three days per week. Technological Chemistry Lectures (second course). Physical Laboratory, 1 day per week, or Advanced Mineralogy Lectures and Practical Course. Mechanical Drawing, Practical (evening class).

Fourth Year.—Organic Chemistry Lectures. Technological Chemistry Lectures (third year's course). Chemical Laboratory, 4 days per week. Mechanical Drawing, Practical (evening class).

Fees.—Every student is required to pay on admission an entrance fee of £1 1s. and a library fee of 5s., and the fees for the classes for which he enters. As alternative courses are in some instances open to a student offering himself for the Victoria University Examinations, it is not practicable to give tabular statements of the fees for every combination of classes. Special prospectuses may be obtained at the office of the College.

Certificates will be granted to students on the successful completion of this course. Attendance on the full course of four years is expected of candidates for the Certificate, but students may obtain exemption (on cause shown) from the first or the first and second year's courses. Students so excused will nevertheless be required to undergo examination in all the subjects specified. The Certificate will state in which subjects the candidate has gained Honours, and in which he has merely satisfied the Examiners.

UNIVERSITY COLLEGE, NOTTINGHAM.

Department of Chemistry.

Professor of Chemistry—Frank Clowes, D.Sc. Lond., F.I.C., F.C.S.

Demonstrators.—J. B. Coleman, F.I.C., F.C.S., and R. L. Whiteley, F.I.C., F.C.S.

Lecturers.—J. B. Coleman, F.I.C., F.C.S., R. L. Whiteley, F.I.C., F.C.S., C. Haydon White, M.R.C.S., J. W. Carr, B.A., and F. R. Sargeant.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1889-90 will be as follows:—First Term, October 7th to December 21st; Second Term, January 20th to April 3rd; Third Term, April 14th to June 28th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry in the third term. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes, 50s. for the session of three terms: Non-Metals or Metals 42s.: Organic Chemistry (one term) 21s.: Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees.—For one term, £6; for the session, £15; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Dyeing and Bleaching, Brewing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A Pharmaceutical Curriculum extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), and Practical Dispensing, taught by demonstrations and practical work in the laboratory.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonrator of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 2s. 6d.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, B.Sc., F.C.S.

The Session will commence on Tuesday, October 1.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Friday, from 10 to 11 a.m. Fee, £3 13s. 6d.

Second Year's Course.—Chemistry of Metals. Tuesday and Thursday, from 10 to 11 a.m. £2 12s. 6d.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.; Second and Third Courses together, £4 4s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Monday and Wednesday, 6 to 9. Sessional Fee, one evening per week, £1 10s.; two, £3; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

Professor. — Percy F. Frankland, Ph.D., B.Sc., F.I.C., &c.

Lecture Assistant.—Andrew Thomson, M.A., D.Sc.

The seventh session of the College will be opened on October 5th, 1889.

The Lectures and Laboratory practice in Chemistry are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the University of St. Andrews and Edinburgh.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: Inorganic Chemistry (Non-Metals), Monday, Wednesday, and Friday, from 10 to 11 a.m.; fee, £2 2s.

Second year's lecture course: 1. Inorganic Chemistry (Metals), Tuesday and Thursday, from 9 to 10 a.m.; fee, £1 11s. 6d. 2. Organic Chemistry, Tuesday, Wednesday, and Thursday; fee, £1 11s. 6d.; fee for the entire year's course, £2 2s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also suitable for students preparing for their medical and pharmaceutical examinations. A three months' course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction.

UNIVERSITY OF EDINBURGH.

Professor.—A. Crum Brown, F.R.S.E.

Two degrees in Science are conferred by the University of Edinburgh, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.). Both these degrees are conferred in Physical and Natural Science, in Public Health, and in Engineering.

Candidates for degrees in Physical and Natural Science must pass a preliminary examination in English, Latin, Arithmetic, the Elements of Mathematics, and the Elements of Mechanics, and in at least two of the following subjects:—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, and Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, including Comparative Anatomy, and Botany. The Second B.Sc. Examination the Higher Mathematics, Experimental Physics, Chemistry, Zoology, Botany, Physiology, and Geology, including Palæontology and Mineralogy.

The D.Sc. Examination embraces Mathematics, Natural Philosophy, Applied Mathematics, Experimental Physics, Practical Astronomy, Chemistry, Zoology and Comparative Anatomy, Animal Physiology, Botany, and Geology, including Palæontology and Mineralogy.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886,

according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

The Chemical Laboratory (Prof. Dittmar's) opened on September 2nd. The Lecture Courses commence on October 1st.

Copies of the Calendar for 1889-90 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry. — T. Purdie, B.Sc., PH.D., Assoc. R.S.M.

The Session begins on October 29th. A Competitive Examination, open to intending Students of Arts or Science, for nineteen Entrance Bursaries, ranging in value from £30 to £10 each per annum, will be held on Friday and Saturday, October 25th and 26th. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the "University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, forming an introduction to the discussion of Chemical Theory; the Non-metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supplementary Lectures, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £10 10s. for the Session. Shorter Courses of Practical Chemistry will be arranged to meet the requirements of Students who cannot give so much time to the subject, the fees for which vary according to the number of hours taken weekly.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—Maxwell Simpson, D.Sc., M.D., F.R.S., &c.

The Course of Theoretical Chemistry is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry and Crystallography, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Thence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

The Course of Practical Chemistry consists of about thirty-nine Lectures, and will commence at the beginning of the Second Term. Fee for each Sessional Course £3.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, Stephen's Green, Dublin.

Professor of Practical and Theoretical Chemistry.—W. N. Hartley, F.R.S.

The Session commences on Monday, October 7, 1889.

The instruction comprises courses of Lectures on General, Applied, and Analytical Chemistry, and also a course of Lectures on Metallurgy.

The Chemical and Metallurgical Laboratories, under the direction of Professor Hartley, are open every week-day during the Session. Instruction is given in the different branches of Analytical Chemistry, including Assaying, and in the methods for performing Chemical Research. Fee, for the Session of nine months, £12; for six months, £9; for three months, £5; for one month, £2. Fee for a course of assaying not less than £5.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are given to Associate Students, not being Royal Exhibitioners, who have been a year in the

College on the results of their examinations. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Science Examinations of the Department of Science and Art.

A Diploma of Associate of the College is granted at the end of the three years' course.

Evening Classes.—Courses of Evening Lectures are occasionally given by the Professors during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examination will be held on Monday, September 23rd. *Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. The Instructors in the workshops are skilled craftsmen. All the Teachers of the Trade Classes are men who have worked at their industry as foremen. The Session is divided into three terms:—The Winter term commences on Tuesday, October 8th. An examination for the admission of Students will be held at the College at 10 o'clock on Wednesday, October 2nd, 1889, and the work of the Session will commence on October 8th.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane.—*Chemistry:* Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6—8 p.m.; Thursdays, 8—10 p.m.; Saturdays, 7—9 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 7.30 p.m.; Advanced, Wednesdays, 8.45 p.m.; Practical, Wednesdays, 6—7.30 p.m.; Fridays, 6—10 p.m.

School of the Pharmaceutical Society of Great Britain, 17, Bloomsbury Square, London, W.C.—Professor of Chemistry, Wyndham R. Dunstan, M.A., F.C.S. Professor of Practical Chemistry, John Attfield, Ph.D., F.R.S. In this school, which is specially intended for Pharmaceutical Students, Courses of Instruction are given in the sciences of Chemistry (Physical, Inorganic, and Organic) and Botany, as well as in their applications to Pharmacy and Medicine. Professor Dunstan delivers during the Session (October to July) two Courses of Lectures on Chemistry; an Elementary Course from October to April and an Advanced Course from April to July. The Laboratories for practical instruction in Chemistry under the direction of Professor Attfield are open daily throughout the Session. The Research Laboratory of the Society, under the direction of Professor Dunstan, is open without payment to properly qualified persons who are desirous of conducting pharmacological and chemical investigations. Particulars respecting Scholarships, Medals, and Prizes, as well as other information relating to the School, may be obtained on application.

Charterhouse Science and Art Schools.—The Winter Session will commence on Saturday, September 28th, 1889, under the presidency of the Rev. H. Swann, M.A. Classes are established in this institution by which instruction of a practical character is given in most of the Sciences at a very nominal fee; whilst in Art, at an equally low rate, Students, under the direction of five competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will also be held to prepare Candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), Legal, and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well-fitted Laboratory, capable of accommodating sixty Students. Aspirants for University Honours can at a small expense be assisted in their studies.

The City School of Chemistry and Pharmacy, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, and Therapeutics.

New Central School of Chemistry and Pharmacy, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

South London School of Pharmacy, 325, Kennington Road, S.E.—This School opened on September 16th, and the Session lasts until July 15th, 1890. Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S, assisted by Mr. Armstrong. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £10 10s. (junior) and £12 12s. (senior); afterwards £2 2s. and £3 3s. per month respectively, inclusive of all departments.

Polytechnic Institute, 309, Regent Street, London, W.—Special Courses of Lectures on (*a*) the Manufacture of Painters' Oils, Colours, and Varnishes; and (*b*) Oils and Fats, including Candle Manufacture, will be delivered on Tuesday Evenings during the winter by Mr. J. G. McIntosh, commencing on Tuesday, October 1st, at 8 p.m. Classes for practical instruction in these subjects under the immediate superintendence of the Lecturer will also be formed. For further particulars apply to Secretary.

Onslow College of Science, 183, King's Road, Chelsea, S.W.—Lectures and Laboratory instruction in Chemistry and Pharmacy. Special Evening Classes in Inorganic and Organic Chemistry, Metallurgy, &c. The Chemical and Metallurgical Laboratories are open every day and evening for practical work. Principal, Mr. W. H. Martin.

Royal Victoria Hall, Waterloo Bridge Road, S.E.—Science and Technical Classes, Session 1889-90. Lectures will be given in the following subjects:—Principles of Chemistry, Electricity and Magnetism, Heat, Light, and Sound, Biology, and Mechanics. The instruction given is suited to artizans and practical men, and is chiefly in connection with the Science and Art Department, South Kensington.

Portman School of Pharmacy, 156, Marylebone Road, Regent's Park.—Principal, Mr. F. H. Painter.

University Correspondence College, 1, Strand Hotel Buildings, Booksellers Row, W.C.—Specially prepared Courses of Lessons are given for the Examinations of the University of London.

Westminster College of Chemistry and Pharmacy, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton.

Bristol Medical School.—Mr. T. Coomber, F.C.S.

Institute of Chemical Technology, Hackins Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

Leeds School of Medicine.—Prof. Smithells.

Leeds School of Science and Technology.— Mr. J. Wertheimer, B.Sc., F.C.S., and Mr. E. Rawlins, F.C.S. Day Classes for ladies and gentlemen in Practical Chemistry and in Chemical Physics.

Manchester Technical School. — Lecturers: Dr. Gibson Dyson, F.C.S., Mr. E. Bentz, F.C.S., and Dr. T. T. Best. The day classes commenced on Sept. 2nd, 1889, and the evening classes will commence on Sept. 23rd. The school is equipped with two large laboratories for the practical study of Pure Chemistry and Physics, a Laboratory for Metallurgy, and one for Dyeing, Bleaching, and Printing. Special practical work in any branch of Chemical Technology, or in preparation for University Examinations, will be arranged to suit individual Students. The Evening Courses of instruction are esgecially designed to meet the wants of those already engaged in various industries. A syllabus, containing full particulars as to hours, fees, &c., may be obtained from Mr. J. H. Reynolds, The Technical School, Manchester.

Newcastle-on-Tyne School of Science and Art and Technical College (Chemical and Metallurgical Department).—Principal, P. Hawkridge, B.A. Lecturers and Demonstrators, W. D. Oliver, F. N. Cook, H. Oliver, J. D. Best, W. Carr, and J. P. McVie.

Institute of Science and Art, Municipal Buildings, Reading.—Head Science Master: Alfred J. Shilton, F.C.S. Session begins first week in October.

Sheffield Borough Analysts' Laboratory, 1, Surrey Street. — Mr. A. H. Allen, F.C.S. Day and Evening Classes.

Sheffield Mechanics Institution, Tudor Street.—Lecturer on Chemistry, Henry J. Hardy, F.C.S., &c. The Course is divided into Organic and Inorganic Chemistry. About 30 Lectures are given in each. The Session commences September 26th.

Public Laboratory, 34, Bank Street, Sheffield.—J. O. Arnold, F.C.S., and Henry J. Hardy, F.C.S. Day and Evening Classes. Special Classes in Iron and Steel Analysis.

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THE CHEMICAL NEWS.

Vol. LX. No. 1557.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.*

By Sir LOWTHIAN BELL, Bart., F.R.S., F.C.S., D.C.L., M.Inst.C.E., President of the Section.

It has occasionally been the practice of former occupants of this chair to devote a considerable portion of the presidential address to the more recent discoveries in chemical science. This branch of learning advances now with such rapid strides and covers so wide a field, that no one who has not made it the business of his life can hope to discharge this duty with even a moderate share of success.

My immediate predecessor, indeed, discouraged any further attempts in this direction on the ground of the impossibility of doing it justice within the limits of a short discourse, and his remarks were consequently directed to the best methods of teaching the science with which Section B is more directly concerned. I propose this morning to add my testimony to the importance of Dr. Tilden's recommendation, by comparing the rate of progress of one of our great national industries as it has been advanced with and without the aid which chemistry is capable of affording. For this purpose I have selected the metallurgy of iron, not only from my greater familiarity with its details, but because, in my judgment, it affords a suitable example for the object I have in view.

It is needless to insist on the disadvantage attending the application of a science to practical work, without a fair knowledge of the principles which regulate its action. At the same time it would be unfair to those who were engaged in the manufacture of iron during the first half of the present century to deny the value of the services rendered to their art, without giving much thought to the laws of nature upon which their processes depended. The work so performed sufficed, nevertheless, to place the world in possession of the metal in such abundance and at so low a cost that no engineering works have been delayed on account of the high price of or absence of the required quality in the produce of our ironworks during the period in question. On the other hand, it is not to be denied that since the iron-masters have allied themselves with the chemist they have made more progress in thirty years than their predecessors did in three centuries.

No one unacquainted with the archæology of the iron trade could suppose that the colossal furnaces pouring forth their streams of molten metal, followed by the rapid action of the Bessemer Converter, were the modern representatives of the iron-making appliances of former days. Out of the latter, in a low hearth not larger than a domestic fireplace, often dependent on the wind for their blast, a few pounds of ore were at a considerable cost for labour, fuel, and waste of metal, converted into malleable iron. By means of a modern furnace, in an hour and a half a ten-ton converter can be filled with liquid cast-iron, which in twenty minutes may be run into ingots cheaper, stronger, and more malleable than the best wrought iron of our ancestors, or indeed of our own manufacture.

How out of the small fire of the ancient ironworks the German Stück-Ofen was evolved is a matter of conjecture. In both, owing the conditions under which the fuel was burnt, carbon dioxide was largely the product of its combustion. The oxidising property of this gas was in each the cause of the waste of metal just spoken of. Probably, and for other reasons than avoiding this loss of iron attempts were made to increase the dimensions of the Stück-Ofen. If this addition were one of limited extent, the smelter would find, to his cost, that a substance was obtained which no longer possessed the malleable property of that obtained from the lesser furnace. This change would be due to the absorption of carbon, but not in sufficient quantity to constitute that valuable form of the metal known as cast-iron. With a material useless for the smith and incapable from its difficult fusibility of being run into moulds, we can understand the delay which took place in the introduction of the blast furnace which about the middle of the sixteenth century gave to cast-iron a recognised and valuable position in the arts.

In those days there was no very exact science to appeal to, for two hundred and fifty years after the "high furnace" of the Germans and French had been set to work, Fourcroy in his "General System of Chemical Knowledge and its Application to the Phenomena of Science and Art," arrived at the conclusion that cast metal was erroneously supposed to be a mixture of slag and iron or a compound of arsenic or manganese and iron. This was written in 1804 in a work of five thousand pages, when he leant to the opinion that Monge and Berthollet were more correct in considering the product of the blast furnace as consisting of iron, oxygen, and carbon.

When the malleable iron-maker had placed in his hands a material containing, as the pig did, more than 90 per cent of metal, he found it greatly to his advantage to avoid having to deal with all the earthy matter contained in the ores, for it was the presence of silica and alumina which helped to add to the waste incurred in the old hearths. The object sought for in the old Catalan fires, as they were called, in treating ore was one of a reducing or deoxidising character, whereas the reverse of this was required when ore was replaced by pig-iron. In the first, oxygen had to be removed from the oxide of iron, in the latter oxygen had to be united with the metalloids found in the pig. These were distinctions unknown in the days we are considering, and therefore did not trouble the minds of the iron-masters. In both cases there was a large formation of oxide of iron, and when pig-iron was handed over to the Catalan furnace man, it was the oxide of iron so generated which performed the desired duty, and thus this simple mode of procuring malleable iron remained undisturbed for upwards of two hundred years.

The discovery which led to the discontinuance of the low blast furnace as a means of procuring iron in its malleable form was that of puddling made by Cort in 1784. In point of fact Cort's process was merely doing in a reverberatory furnace that which was previously effected by means of compressed air. In an economic point of view, however, the difference is great, and its consequences were of immense importance; for to the puddling furnace we were first indebted for an ample supply of cheap iron by which, in a variety of well-known ways, the interests of the human race have been so largely promoted. As an indication of the indifference of those formerly engaged in industrial pursuits to the scientific aspect of their calling, may be mentioned the fact that puddling had been largely followed for upwards of half a century before it occurred to anyone to examine the chemistry of the process.

Down to the beginning of the seventeenth century the only fuel used in the blast furnace, and, indeed, in the manufacture of iron generally, was charcoal. In 1620 Dudley made several attempts to substitute mineral coal for vegetable fuel in his smelting works, which, by the exhaustion of timber, had become very expensive. He failed in this, and in consequence the British iron trade gradually fell until it was not equal to the production of one modern blast furnace. This happened in 1740, when Darby, by treating pit coal in the same fashion as the charcoal burners had done with wood, *i.e.*, by charring it,

* Read Thursday, September 12 1889

restored vitality to an expiring industry. It is true the restoration must have been of a languid character, for in half a century afterwards it is said the weekly produce of a furnace did not exceed fifteen or sixteen tons.

Various changes were introduced into the manufacture of iron in the first quarter of the present century, but these were rather of a mechanical than of a chemical nature. They chiefly owed their origin to the lessons taught by the chemist Black to James Watt, who profited by them in the application of steam as a motive power. This brings us to the year 1828, a year which will always be distinguished in the annals of the iron trade, by the discovery of Neilson of the value of heated air in smelting the ores of this metal. I never heard it pretended that this inventor had any pretensions to be considered a man of science. Had it been otherwise, the knowledge of the virtues of the hot blast might have been indefinitely postponed, and this opinion is founded on the fact that for many a long year no satisfactory explanation was given why heat obtained by burning coal in the hot air apparatus was capable of saving three or four times its weight in the fuel consumed in the furnace itself. I propose, with your permission, to consider this subject with more attention than I shall devote to other portions of this address, and I am led to do this, not only because it is one of some scientific interest, but because its study seems to afford a solution to some questions in respect to which great differences of opinion prevailed among those whose daily work led them to pay much attention to their details. These questions have all a reference to the quantity of fuel consumed in smelting the ore, as this may be affected by the temperature of the blast and the dimensions of the furnaces employed for this purpose.

As is well understood, the heat excited in an iron furnace may be classified under three heads:—

First, that derived from the combustion of the coke at the point where the blast enters the furnace, the ultimate product being carbonic oxide.

Second, the conversion of a portion of this carbonic oxide into carbon dioxide.

Third, the heat carried into the furnace by the blast.

For the better illustration of the relations which the heat derived from these sources bear to each other, a table (No. I.) has been prepared in which the quantities of each are given in centigrade calories, and reckoned upon 20 units of iron to correspond with English weights. The information upon which the calculations are based is derived from actual observation gathered from furnaces of different sizes and fed with air at different temperatures.

A second table contains statements showing the manner in which the heat so generated is appropriated in the various divisions of the duty the furnaces had to perform, and, for facility of comparison, alongside the quantities of heat so required, their equivalents in the coke used have been added.

In the table, No. II., the appropriation of the heat is separated into *Constants* and *Variables*. The first consists of items where the quantity of heat in making a particular quality of iron is only liable to alterations of trifling amount. On the other hand, the variables exhibit in A and B differences so considerable that work which in in the furnace blown with cold air absorbed 73,388 calories per 20 cwts. of pig-iron was done with 58,645 calories by merely raising the blast to 485°.

The cause of this great variation in the amount of heat required for a given weight of pig-iron, produced under different circumstances as to temperature of blast and size of furnace, depends on changes in the actual amount of work to be performed. How this arises will be best seen in the description of the four examples set forth in the two tables.

Beginning with A, which is a furnace 48 feet in height, blown with cold air, and consuming 45 cwts. of coke and 18 cwts. of limestone per ton of metal, the volume of gas produced may be taken at 14,460 cubic yards at ordinary

TABLE I.

—	A	—	—	—
Height of furnace in feet ..	48	48	80	80
Calories—per unit of coke burnt to CO	2078	2028	2018	2045
Calories from portion of this CO burnt to CO_2	560	1059	1636	1463
Total calories from coke ..	2638	3087	3654	3508
Calories in blast	—	508	534	732
Total heat per unit of coke..	2638	3595	4188	4240
Temperature of blast C. ..	0°	485°	485°	695°
Cwts. blast per ton of metal	228	128	103	94
Cwts. escaping gases per ton of metal	285	170	138	126
Cwts. slag per ton of metal..	34	31	29	28

temperatures and pressures. At the temperature at which they escape we may assume the volume per ton of iron to be about 36,000 cubic yards, passing out of the furnace at the rate of 357 cubic yards per minute.

In comparing the consumption of coal formerly burnt in the hot-air stoves with the saving of coke in the furnace, account must be taken of the different conditions of the combustion. In Table I., owing to the small quantity of carbon dioxide formed, the heat evolved is only 2638 calories per unit of coke, whereas each unit of the coal consumed in heating the air afforded three times this quantity of heat. Doubtless there was a great loss in the operation of heating the air, for it would not appear that much above one-fourth of the theoretical quantity of heat capable of being generated by the coal reached the furnace through the tuyères.

We have now to consider the nature of the change which is effected in a furnace where, for every 2638 calories generated by the combustion of the coke, 508 calories are carried in by the blast. It will be readily understood that with the velocity at which the gases are passing out of the cold-blast furnace they have but little time to impart their heat to the incoming solids, or to have the carbonic oxide they contain converted into carbon dioxide. The withdrawal of so much coke, and its place taken by heat contained in the blast, means that the 14,460 cubic yards of escaping gases are reduced to about 12,120 cubic yards. The effect of this is not only to alter the speed at which the gases are passing through the materials, but to alter the relation in point of quantity which the ironstone present in the furnace bears to the coke, so that in point of fact a larger space is occupied by the ore than was before, and a lesser one by the fuel. We have thus the carbonic oxide passing more slowly over the oxide of iron at the same time that there is a greater quantity of the oxide exposed to the influence of the reducing gas. To illustrate how this operates, a table has been prepared showing how each 1000 cubic feet of furnace space is occupied in the four cases we are considering:—

	A. 48 feet cold blast.	B. 48 feet hot blast.	C. 80 feet blast.	D. 80 feet blast.
Coke cubic ft. ..	736	686	590	590
Limestone ,, ..	63	75	86	77
Ironstone ,, ..	201	239	324	333
	1000	1000	1000	1000

The immediate effect of the introduction of the hot blast is to alter the spaces filled by the three minerals from those given in Column A to coke 686, limestone 75, and ore 239 cubic feet. This is followed by a twofold advantage. Volume for volume, ore and limestone possess double the heat-intercepting power of coke, and there is 19 per cent more ore ready to oxidise the carbonic oxide passing over it at a reduced speed of 16 per cent than there was when using cold air. The increased efficiency of the coke, due to a more perfect cooling of the gases and higher oxidation of the carbonic oxide, permits

TABLE II.

Showing the appropriation of Heat and its equivalent per ton Iron.

Appropriation of heat per 20 of pig-iron.	A—Blast 0° C.		B—Blast 485° C.		C—Blast 485° C.		D—Blast 695° C.	
	Calories.	Cwts. coke.	Calories.	Cwts. coke.	Calories.	Cwts. coke.	Calories.	Cwts. coke.
CONSTANTS: —								
Reduction of Fe_2O_3 in ore	33,108	12·550	33,108	9·209	33,108	7·905	33,108	7·808
Reduction of metalloids in pig ..	4,174	1·582	4,174	1·161	4,174	0·996	4,174	0·984
Dissociation of CO ($2CO = C + CO_2$	1,440	0·546	1,440	0·400	1,440	0·344	1,440	0·340
Fusion of pig-iron	6,600	2·501	6,600	1·836	6,600	1·576	6,600	1·557
Constant calories per 20 of pig ..	45,322	—	45,322	—	45,322	—	45,322	—
Coke consumed per 20 of pig. Cwts.	—	17·179	—	12·606	—	10·821	—	10·689
VARIABLES: —								
Evaporation of water in coke.. ..	630	0·239	411	0·114	312	0·074	298	0·070
Decomposition of water in blast ..	5,420	2·055	3,348	0·931	2,720	0·649	2,408	0·568
Expulsion of CO_2 in limestone ..	6,660	2·526	5,920	1·647	5,054	1·207	4,070	0·961
Reduction of CO_2 in limestone to CO	6,912	2·620	6,144	1·709	5,248	1·254	4,099	0·962
Fusion of slag	18,590	7·045	17,325	4·819	16,720	3·993	15,565	3·673
Carried off in escaping gases.. ..	29,482	11·178	18,486	5·144	11,043	2·636	8,906	2·101
Heat in tuyere water at hot-blast furnaces, loss from walls, &c. ..	5,694	2·158	7,011	1·950	7,057	1·686	9,389	2·216
Variables for 20 of pig	73,388	—	58,645	—	48,154	—	44,735	—
Variables for coke for 20 of pig ..	—	27·821	—	16·314	—	11·499	—	10·551
SUM OF CONSTANTS AND VARIABLES:—								
Calories for 20 of pig-iron	118,710	—	103,967	—	93,476	—	90,057	—
Cwts. of coke for 20 of pig-iron ..	—	45	—	28·92	—	22·32	—	21·24

TABLE III.

Showing the quantity of Oxygen and Carbon in gases per 1000 parts of Pig-iron produced. The eight feet immediately below charging plates is occupied by charging apparatus.

Distance below top of minerals.	0 ft.		8½ ft.		18 ft.		31 ft.		44½ ft.		57 ft.		62½ ft.		68 ft.	
	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.
No. 1. Oxygen ..	1843	—	1250	—	1235	—	1234	—	1236	—	1207	—	1137	—	1348	—
Carbon ..	—	1101	—	864	—	816	—	871	—	904	—	899	—	890	—	967
No. 2. Oxygen ..	1848	—	—	—	1410	—	1482	—	1190	—	1207	—	1255	—	1366	—
Carbon ..	—	1104	—	—	—	914	—	1046	—	894	—	887	—	—	—	927
No. 3. Oxygen ..	1670	—	1309	—	1206	—	1312	—	1256	—	1253	—	1253	—	1378	—
Carbon ..	—	1048	—	926	—	907	—	918	—	946	—	931	—	939	—	1013
No. 4. Oxygen ..	1670	—	1271	—	1224	—	1300	—	—	—	1261	—	1285	—	1387	—
Carbon ..	—	1048	—	897	—	898	—	917	—	—	—	926	—	977	—	1021

NOTE.—Nos. 3 and 4 were using partially calcined limestone, hence the deficiency of O. and C. until the lower depths are reached.

TABLE IV.

Showing what may be regarded as a typical instance of the absence of Carbon Dioxide in the gases taken from a furnace of 80 feet. Measurements taken from the highest level of the minerals, *i.e.*, eight feet below charging plates.

Depth below charge.	Escape pipe.	3½ ft.	9 ft.	16 ft.	22½ ft.	28½ ft.	35 ft.	41½ ft.	66 ft.
Carbonic Acid	16·07	11·71	10·03	8·17	6·12	—	—	0·72	3·01
Carbonic Oxide	27·34	29·71	31·39	31·40	32·79	35·27	36·00	36·02	39·47
Hydrogen	0·11	0·10	0·07	0·14	0·28	0·10	0·11	0·08	0·14
Nitrogen	56·48	58·48	58·51	60·29	60·81	64·63	63·89	63·18	57·38
Total ..	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

its further suppression until the relative spaces filled by the materials are those shown under Column B. These advantages would not of themselves suffice to save 16 cwts. of coke, or thereabouts, out of 45 cwts., but the reduction in the coke consumed is followed by a diminution in the quantity of air used, and in the weight of gases and slag produced. A reference to the appropriation of heat classified under the head of Variables will show in consequence diminution from 73,338 to 54,643 calories.

It may be asked whether this prolonged exposure of the ore to the reducing gases could not be secured by driving the furnace at a lower speed. There is, however, a point which may be regarded as one of equilibrium, in which the quantity of cold materials charged at the top just suffices to reduce the temperature of the gases, leaving it as far as is possible consistent with the dimensions of the furnace. If the volume of blast entering at the tuyères is lowered one-half it would mean that the materials would be exposed for twice the time to the hot gases they were previous to the alteration in the rate of driving. The elevation in the temperature of the coke would enable its carbon to act on the carbon dioxide, so that there would ensue as great a loss under the second head of heat evolution in Table I. as there is gained by a more perfect interception of the heat contained in the gases.

There is, however, another way of securing this prolonged exposure of the ore to the action of the reducing gas without incurring the inconvenience just referred to, viz., by increasing the dimensions of the furnace blown with cold air. When this was done by raising the height from 48 to 71 feet it was found that the duty performed by the coke, apart from the heat contained in the blast, was just about the same as that in the hot-blast furnace.

With regard to the position of equilibrium above referred to, it is worthy of remark that, while this was reached when a furnace of 48 feet ran 100 tons per week when driven with cold air, it was not arrived at in one of similar dimensions using heated air until the make was increased to about 220 tons.

When we proceed to examine the composition and weight of the gases given off by a 48-feet furnace blown with air at 485° C., it will be found that about 20 per cent of the carbon as dioxide has disappeared, due no doubt to the still excessive temperature of the upper zone and too rapid a current of the reducing agent. An obvious way to remedy this evil would be by an addition to the capacity of the furnaces. This was done by raising them to a height of 80 feet, with a cubical space three or four times greater than those of 48 feet. In such a furnace almost the full theoretical quantity of carbon as dioxide has been obtained, but, while the larger furnace held three or four times as much ore, &c., the production was only about double that of the lesser. On referring to Table II. it will be seen that a further economy of 6·6 cwts. of coke has been effected in Furnace C as compared with B, due solely to an enlargement of space, for the temperature of the blast was exactly the same in both. This improvement, it will also be perceived, is due to an extension of those causes which acted so beneficially when hot air was applied to B.

If 6·6 cwts. of carbon, or thereabouts, is the full quantity per ton of iron which can be found in the gases as dioxide, and if, in a furnace working under the conditions of C, it requires 22·32 of coke to furnish this carbon and that in the carbonic oxide, it is clear we cannot withdraw any coke without disturbing the position of equilibrium supposed to have been established in the case of the furnace in question. Suppose into such a furnace the blast, instead of 485°, is admitted at 695° as happened under Column D. The additional heat, 732 calories, instead of 534 as in C, will make itself felt throughout the entire height of the furnace, including, of course, the upper zone. Immediately this happens the carbon dioxide generated by the reduction of the ore attacks the coke and escapes as carbonic oxide. If Table I. is examined it will be seen that almost the whole of the additional heat carried into the furnace D, as compared with C, has been absorbed by the disappearance of carbon dioxide, so that the net power of the coke unit in both cases is practically the same. Nevertheless it will be remarked that there is still a small saving of coke due to a reduced amount of blast, escaping gases, &c.

From what has preceded it has been concluded that a furnace of 80 feet affords sufficient opportunity for the gases being as fully saturated with oxygen as the nature of the process of deoxidising the ore will permit. The sensible heat in the escaping gases, however, still represents a considerable loss, reduced as they have been from 29,482 to 11,043 calories.

According to estimate it was believed that the reduction of oxide of iron ought to be attended by an increase of temperature—in other words, the conversion of carbonic oxide into carbonic dioxide produced more heat than that absorbed by splitting up oxide of iron into its constituent parts. The estimated difference not being a large one, an experiment was made by substituting in the furnace inert substances having about the same specific heat as the ore. The results confirmed the correctness of the calculation—the temperature of the escaping gases fell, and rose to their normal point when the use of ore was re-commenced. A more expensive experiment was subsequently made in the same direction by building, at Ferryhill, a pair of furnaces having a height of 103 feet, without any substantial benefit being derived from the large additional expenditure incurred.

It was Scheerer, I think, who first divided the blast furnace into zones. The first division, beginning at the top and extending twelve feet downwards, was designated the preheating zone; the following eighteen feet downwards was distinguished as the reducing zone; the next eight feet the carburising zone, followed by four feet which constituted the zone of fusion. The lowest of all, having a depth of about six feet, was named the zone of combustion. The author of this mapping out, as it were, the interior of the furnace, does not wish to be understood as confining its various functions within the respective spaces assigned to them; on the contrary, he admits the existence of considerable variations of position. My own observations, however, have led me to conclusions varying considerably from those adopted by Scheerer.

The fundamental cause of these differences seems to depend on the temperature considered as being required for a commencement of the reduction of the ore. By Scheerer the reducing zone is considered to require a temperature of 1000° to 1200° C. This change undoubtedly is not the same with all kinds of ores, but my experiments were conducted when using almost every variety of the mineral. According to the trials made a mixture of one volume of carbon dioxide and two volumes of carbonic oxide at a temperature of 410° removed 10 per cent only of the oxygen in Cleveland ore, and 37·8 per cent from an artificially prepared oxide. The composition of the gases at the different depths, however, indicates in an unmistakable manner the nature of the action which is going on at any particular point. A table has been prepared from actual analyses of the gases which gives the quantity of oxygen present for every 1000 parts of metal produced, and to this is added the weight of carbon they contained. The results vary, but the general inference to be drawn from the observations made on furnaces of eighty feet is that by the time the minerals have passed through a space of eight feet of the depth they have to travel all the oxygen susceptible of removal from the ore in the upper region is found in the gases, the remainder being retained until it reaches the zone of fusion. The same is the order of action in a somewhat modified form which was found to prevail in the case of furnaces 48 feet in height.

On casting the eye along the lines of figures a somewhat remarkable circumstance is apparent, viz., that the quantity of oxygen per 1000 of pig-iron gradually

decreases as the gases ascend until they approach the upper region, when it commences to increase. This had been the subject of observation for many years without any complete explanation being given of its cause. Dr. Percy, among others, bestowed some attention to the circumstance without arriving at any opinion satisfactory to himself. It is a little extraordinary, so far as I have seen, that no notice has ever been taken of the fact that the carbon in the gases followed the same law. While engaged in investigating the action of furnace gases on the ore, a peculiarity was observed previously unknown to me, viz., that large quantities of carbon were deposited by the dissociation of the reducing gas, the action being $2CO=CO_2+C$. Experimentally I ascertained that spongy iron, as well as oxide of iron, was capable of producing the change, and that thirty per cent of carbon dioxide, mixed with the carbonic oxide, arrested the reaction, the temperature at the time being 420°. Dr. C. A. Wright, who subsequently became chief chemist of our laboratory, was asked to continue the examination. The conclusion arrived at was the impossibility of effecting the complete reduction of E_2O_3, or of any oxide, by CO. On the contrary, when metallic iron known to contain no oxygen was exposed to a current of this gas, carbon was deposited and oxygen absorbed. It would seem, therefore, that this absorption of oxygen by the iron and precipitation of carbon suffice to explain the disappearance of these two elements from the gases, and that they remain in this condition until the fusion of the iron, in contact with intensely heated carbon, liberates the oxygen as well as that portion of the carbon which is not absorbed by the metal in order to produce pig-iron.

So far, then, as the analyses given in Table III. enable us to judge, instead of the upper two-thirds of a furnace being required for the purposes of reduction, no material change is effected after passing through 18 feet in a modern furnace of 80 feet in height. After this the composition of the gases, and, therefore, of the minerals, remains pretty steady until the vicinity of the tuyères is reached, with the consequences already referred to.

Of the excess of oxygen at the zone of combustion it is highly probable that a portion is due to the reduction of P_2O_5, SiO_2, SO_3, and CaO. In the case of Cleveland iron I have estimated this at 54 parts per 1000 of pig-iron produced, but the average total oxygen beyond that furnished by the blast in the first two instances given was 130 parts. At this rate there must have been 76 parts of oxygen liberated from the oxide of iron, which is equal to 19 per cent of that originally combined with the iron in the ore.

It may be appropriate here to refer to what may be taken as a typical expression of the working of a blast furnace in respect to the presence of carbon dioxide. An analysis of the gases is therefore inserted, drawn from an 80-feet furnace at various levels, with the simple remark that it is improbable that carbon dioxide can exist for any length of time when exposed to incandescent coke at the temperature which prevails at the depths mentioned in the last two columns.

Something like forty years ago the escaping gases from the blast furnaces, rich as they were in carbonic oxide, were permitted to burn wastefully on the surface of the minerals charged at the throat. This meant a loss of about 54 per cent of the heating power of the coke. For reasons already given it was of course impossible to utilise much of this heat in the actual smelting of the ore, because of the necessity of preserving a large excess of carbonic oxide in the gases. This, however, constituted no reason why, apart from the furnace work itself, this vast quantity of gaseous fuel should not have been utilised, as it no doubt would earlier have been, had the ironmakers known, as they now do, its full value. To-day all the blast and other engines are driven and the air is heated at our blast furnaces by fuel formerly wasted, and this without any labour for stoking being required. In Great Britain alone the annual saving is fully equal to four million tons of coal.

In connection with the other volatile products which accompany the iron smelter's work I will only mention ammonia. Some qualities of coal admit of being used in the raw state. In this case, as in distilling coal for illuminating purposes, ammonia is generated and may be collected. Instead, however, of the ammoniacal vapour being all contained in the hydrocarbons, as in gas-making, it is diluted in addition with all the fixed carbon as oxides and all the nitrogen of the atmospheric air used in its combustion. Nevertheless, Messrs. Bairds, of the Gartsherrie works, and others, are manufacturing large quantities of ammonia sulphate from the ammonia so obtained. A similar object is achieved by attaching the necessary condensers to the apparatus for coking coal. The process of distillation is then carried on in hermetically closed ovens heated by the combustion of the gases evolved. These, before reaching the fire-place where they are burnt, are deprived of their ammoniacal vapours by passing through condensers provided for the purpose. Previous, however, to this being done, the waste heat from the coking process had been applied for generating steam, so that at certain collieries in the county of Durham all the mechanical power is obtained without any coal being specially burnt for this purpose.

Before speaking of the next and last great improvements in connection with my subject, I should like to say a few words, and a few words only, respecting steel, a well-known and most valuable compound of iron and carbon. Let me first observe that it seems improbable that this substance was not earlier known to the ancients, as was at one time supposed. The facility with which the metal combines with carbon renders it very unlikely that acieration would not occasionally take place when iron itself was the object of the manufacturer. Certain it is that Agricola, who wrote in 1556, describes in Latin a mode, apparently as well known as that of making iron itself, of making *Acie*. The engraving in his "De re Metallica" shows bars of malleable iron placed upright in a charcoal fire resembling that of a Catalan hearth. These, after an exposure of several hours to the incandescent charcoal and hot carbonic oxide, were found changed to steel and employed as such.

After the invention of the blast furnace pig-iron was placed in a similar hearth, and while in a melted state a blast of air was directed upon the molten metal, until just as much carbon remained with the iron as constituted steel. This mode of procedure continued to be practised long within my own recollection, and may, for what I know, still be followed in some districts. The subject of steel-making occupied the attention of Hassenfratz, of Réaumur, and others, but practically the only process followed until 1865 was the well-known one of cementation.

Since the days of Fourcroy it was ascertained that in addition to the iron carbon was an essential ingredient in cast metal, but invariably accompanied by more or less silicon, and whenever the minerals contained sulphur or phosphorus these metalloids were also present. The nature of the actions employed for ridding the product of the blast furnace of these substances so as to render it malleable had also been carefully examined and explained by the light of scientific investigation. The manufacturer had, it is true, learnt by experience and observation how to produce an article of excellence without much knowledge of the science of his art. Among other things he ascertained that to obtain a ton of wrought iron he required the heat of an equal weight of coal in the puddling furnace; but he did not know, nor did even men of science, I think, ever dream, that the oxidation of the metalloids in the pig-iron, and that of a small portion of the metal itself, would afford heat enough to enable the workman to dispense with the use of all coal in the process of conversion. When, therefore, the iron trade was informed in a paper read before the British Association in 1856, entitled "A Mode of Making Iron without the Use of Fuel," its author, Henry Bessemer, was set down by the

iron trade as a deluded enthusiast. At that period I doubt whether ten pounds of wrought iron had ever been seen in a state of fusion at one time. Bessemer, in his description, however, spoke of melting tons of it with no more heat than that afforded by the rapid oxidation of about 5 or 6 per cent of the weight of the pig-iron used. Not only, therefore, was the subject one of economic, but also of high scientific interest. Nevertheless, a mere statement of the title of the paper was all the notice bestowed by our predecessors in their *Transactions* on a discovery which has revolutionised the art of making iron. It is quite true that for some time it appeared as if the scientific aspect of the question were to constitute its only recommendation, for the malleable iron made in a Bessemer converter proved unmanageable when hot, and destitute of strength when cold. Finally, it was ascertained that phosphorus was the source of the evil, and, further, that while carbon and silicon could be almost entirely removed from the molten metal, this third metalloid remained unaffected by the treatment. The extent to which the hurtful influence of phosphorus makes itself felt in the wrought iron obtained by the Bessemer process is somewhat remarkable, because while two- to three-tenths per cent is often present in puddled bars of fair quality, probably no consumer would accept Bessemer steel when it contains half of this amount. The first success was obtained in Sweden, where, by using pig-iron containing a mere trace of the objectionable substance, a product was obtained which was satisfactory. For many years the beneficial effect produced by manganese on steel had been well known, and it occurred to R. F. Mushet, son of David Mushet, one of, if not the earliest scientific metallurgist in the United Kingdom, to try its influence in the converter on iron made from the hematite iron of the West of England, which contained from 0·05 to 0·1 per cent of phosphorus. This addition, apparently by its removing occluded or combined oxygen in the molten iron, afforded the necessary relief, and the operation being one of extreme simplicity, enables steel or wrought-iron to be produced at a greatly reduced cost. To such an extent has this been carried that ore is brought by sea over a distance of 1000 miles to Middlesborough, and from it steel rails are made more cheaply than a greatly inferior article of iron can be produced from the abundant and economically wrought bed of ironstone found within a couple of miles of that town. As an example of the facility of conversion may be adduced the fact that the molten metal is brought direct from the blast furnace, turned into steel or ingot iron as the case may be, and the heat evolved by the operation is sufficient to enable the product in many cases, without further use of fuel, to be taken direct to the mill and rolled into a finished bar.

We have just seen that 0·1 per cent or thereabouts of phosphorus renders steel or ingot iron valueless; in like manner very insignificant variations in the quantities of carbon or silicon materially affect their quality. Now the blow, as it is termed, in a Bessemer converter may be accomplished in from twelve to fifteen minutes. It is clear, therefore, the opportunity of ascertaining the precise quality of the steel is one of very short duration. It is, I think, not disputed that a product can be obtained by this process possessed of very high, if indeed not of the highest, excellence, but it is also pretended that the quality is not sufficiently uniform for certain purposes. The ordinary reverberatory furnace is incapable of affording the necessary temperature for melting steel or wrought-iron, but by employing the fuel in a gaseous state, and by heating the air and gas before they are brought together, as is done in the valuable furnace suggested by the Messrs. Siemens, the heat is so intensified that wrought-iron in it is rapidly fused. Steel is now largely made in such furnaces, either by mixing wrought and cast-iron, as proposed by M. Pierre Martin, or by means of cast-iron alone, when the carbon is removed by the addition of iron ore and some limestone, in which case, by the agency of the ore, the metalloids are oxidised and removed from the bath of iron. Some hours being required for this, sufficient opportunity is afforded for ascertaining the progress of the operation.

The cause of the iron in the Siemens furnace, as well as in the Bessemer converter, retaining its associated phosphorus in time began to attract the attention of chemists. In each case the expulsion of the metalloids is effected by oxidation. The carbon is gasified, and the silicium, on being acidified, is absorbed, and forms a slag containing usually 45 to 50 per cent of silicic acid. In the presence of such an excess of this substance any phosphoric acid, if formed, could not be absorbed by the slag. It was the late M. Grüner, of Paris, who, in 1867, first pointed out this fact, and he it was who first recommended the use of lime in order to render the slag basic instead of acid. Further, in order to avoid the presence of silica, he recommended at the same time that the converter should be lined with lime instead of with fireclay.

The same subject engaged my own attention, when guided by the fact that, as oxide of iron in the puddling furnace was capable of acidifying and removing a large quantity of the phosphorus as iron phosphate, it might be possible, by keeping the temperature of the metal below that required for the process of puddling, to make this removal more complete. The result of these experiments was communicated to the Iron and Steel Institute in March, 1877, when it was shown that pig-iron containing 1·75 per cent of P could, in a few minutes, have this reduced to 0·2 per cent. This process is now being used in the United States for freeing cast-iron from its associated phosphorus.

The rapid destruction of the ordinary Bessemer converter led Mr. G. I. Snelus to consider the practicability of using a lime lining, and on experimenting with this on a working scale he confirmed the opinions previously enunciated by Grüner by observing that the presence of lime had removed a considerable quantity of the phosphorus. These discoveries constitute the foundation of the very important basic process of Messrs. Thomas and Gilchrist, which consists in adding lime to the molten steel in a converter constructed on the principle described by Mr. Snelus. Considerable difficulty had, however, been experienced by this metallurgist in the attachment of the lime lining to the walls of the converter. This important question was solved by Mr. Edw. Riley by exposing dolomite to a very high temperature in order to prevent further shrinking, and then grinding and mixing the powder with coal-tar. This formed a species of cement, which is applied to the sides and bottom of the converter in the form of bricks or as cement. Doubtless, simple as the idea is, it has greatly contributed to the success of the basic process.

The acidification and subsequent transference to the slag of the phosphorus by the basic treatment has led to its application to agriculture. For this purpose the slag is ground to a fine powder and sprinkled over the land without any further preparation. By this operation an indispensable element of animal life is derived from the remains of living creatures which, ages ago, found a grave in the ferruginous mud destined to become the great Cleveland bed of ironstone.

Before closing this portion of my official duty I cannot refrain from tendering to chemists an assurance of the great advantage the manufacturers of iron feel they have derived from the lessons taught them by chemical science. I am the more anxious to do this because we, among others, have been reminded that we are losing the supremacy among industrial nations we once enjoyed for want of that knowledge of chemistry which is more assiduously cultivated abroad than it is in our own country. I am not prepared to deny that the opportunities for acquiring a scientific education are less generally spread here than is the case in France, Germany, or Belgium; but for this the nation, and not the iron trade in particular, is responsible. It must also be ad-

mitted that as manufacturers we no longer stand so far above other lands as we formerly did. In this result any differences of education are in no way concerned, for if I were to classify the nationalities of the various inventions enumerated in the course of my remarks the fears of those who are alarmed at the appearance of a Belgian girder or a German steam-engine on our shores would, I think, be allayed. Perhaps I might be allowed to offer a very few words on the technical side of this important question of education. Much I shall not be able to say, because I have not yet been able to learn the precise position the subject occupies in the minds of its most earnest advocates. If it means, as is sometimes alleged, a system by which, along with scientific instruction, manual dexterity in the use of tools or a practical knowledge of various manufacturing processes has to be acquired, I confess I am not sanguine as to the results. Certain I am that if foreign workmen are more skilful in their trades, which, as a rule, I doubt, and which in the iron trade I deny, this superiority is not due to scientific training in the manner proposed, for in this they possess, so far as I have seen, no advantage over our own workmen. My objection to the whole system is the impossibility of anything approaching a general application being practicable. I have not a word to say against the rudiments of science being taught wherever this is possible. The knowledge so obtained may often give the future workman a more intelligent interest in his employment than he at present possesses, but I think they who expect much good to attend such a thin veneer of chemistry or physics do not take sufficient account of the extent of the knowledge already possessed by more highly educated men who are now directing the great workshops of the world. It is by extending and enlarging this that substantial aid has to be afforded to industry and science, and not by teaching a mere smattering in our primary or any other schools. In the case of young people who, from necessity, must leave the schoolroom at an early age, my own leaning is towards the present system, with the addition of drawing and some natural science. By it certain important lessons are taught, which, if not followed under the discipline of the schoolmaster, run some risk of being entirely neglected. After this, probably, the playground will be found more useful and much more popular with schoolboys than trying to learn a trade by means of tools which, before he has to use them in earnest, may be thrown into the scrap heap.

As a national question, the attention of the Government, Imperial or municipal, ought to be directed to the importance of establishing in all great manufacturing centres institutions resembling that of the Physical College of this city. These should consists of appropriate and even handsome buildings, properly furnished with all the instruments and appliances required for teaching the sciences in their practical bearings on industrial pursuits. In Newcastle, as well as in other places, this has been done on a fairly ample scale, and the advantages the College of Science in this city are capable of affording are offered on such terms that no one can plead expense being a barrier to mental improvement.

Bearing in mind the importance of the subject, and remembering, as my colleagues and myself do, the difficulties we have had to encounter and those we have still before us, I am strongly of opinion that the erection and maintenance of colleges of science should not be left to the accidental liberality of the few, but should be taken in hand by the nation at large.

The Passivity of Cobalt.—Ernest Saint-Edme.—The so-called *passive state* of iron and of nickel is merely a chemical property possessed by their nitrides. This state of passivity is connected with the degree of affinity of the metal for nitrogen, *i.e.*, in a decreasing order for iron, nickel, and cobalt.—*Comptes Rendus*, Vol. cix., No. 8.

THE "AMINES" SEWAGE PROCESS.

ON September 18 we had the pleasure, in company with a very numerous gathering of experts, journalists, and municipal officials, of witnessing the working of this new process at the Wimbledon Sewage Works. The idea of using crude trimethylamine—in other words herring-pickle—for the treatment of sewage seems to have been first entertained by Samuel Walter, who obtained an English patent, No. 5283 of A.D. 1882, in which he claims "adding herring-brine or *sea-salt* to sewage or other foul waters"; and in the body of his specification he mentions that such herring-brine or salt is to be diluted with lime-water.

On October 24th, 1888, Herr H. Wollheim obtained a patent (No. 15,321) in which he proposes to treat the sewage with milk of lime to which trimethylamine or an isomer has been previously added. This inventor seems to have a more distinct aim in view than S. Walter, who possibly uses herring-brine merely as a cheap waste form of common salt. Herr Wollheim, on the contrary, evidently recognises the trimethylamine present in the herring-brine as the active ingredient.

The process which we witnessed was as follows:—Milk of lime was mixed in the proportion of about 4½ lbs. per 1000 gallons, along with about 18 ozs. of trimethylamine. It does not sufficiently appear whether these 18 ozs. are to be actual trimethylamine, or brine, &c., in which such a quantity of trimethylamine has been found to be present.

On the addition of this mixture to the sewage precipitation was rapid. Samples of the effluent dipped up for inspection were fairly inodorous and colourless. They were, however, strongly alkaline, as were also the deposit or sludge and its drainings.

Occasionally, in walking about the works, we encountered a disagreeable smell, not excrementitious nor briny, but rather fishy, such as is commonly experienced where sewage is treated by any alkaline process. We are not, however, free to lay this odour to the charge of the "Amines" process, since in a closely adjoining set of tanks the ordinary Wimbledon treatment was at work "for the sake of comparison,"—a most unfortunate arrangement. Some sludge which had been laid out in a tank ever since August 23rd was submitted to examination. In colour and texture it was very like a lime deposit, but it was without the disagreeable smell which such sludges always have.

Such are the points which were to be seen, and which were shown, without any reservation. In a circular which was distributed, and in an address delivered by Mr. Ellice-Clark, C.E., the Engineer to the "Amines" Syndicate, we were informed that by this treatment the sewage was completely disinfected and "sterilised," all microbia being entirely destroyed. This result, which is vouched for by Dr. Klein, is extremely interesting. This eminent bacteriologist found 2,400,000 organisms per c.c. in a sample of sewage, whilst in some of the same sewage, after treatment by the "Amines" process, there remained none at all. This is the more curious as Mr. A. Winter Blyth, M.R.C.S., in a paper entitled "A Study of Disinfectants by New Methods," communicated to the Royal Society in 1886, found that the amines had but feeble disinfecting powers. Here there is evidently need of further research.

We were also told that the effluent from the "Amines" process underwent no secondary fermentation — an important point on which nothing could be ascertained during a few hours' inspection. If this is the case in an alkaline liquid, *i.e.*, under circumstances most favourable for the production of microbia, the disinfecting powers of trimethylamine must be strong and persistent beyond comparison.

It is to be regretted that in the circular distributed among the visitors no chemical analysis was given either of the effluent or of the dry deposit. This is an important

omission, since a water, though absolutely sterilised, may be utterly unfit either for domestic or industrial purposes. For the waste waters of manufactories, disinfection is, indeed, a very secondary matter.

Some of the advantages attributed, however truthfully, to this process are shared by other methods of sewage treatment. Thus the removal of suspended matters, organic or inorganic, is very generally effected. We were told that fish can live in the effluent from the "Amines" process if previously diluted with ten vols. of river water. But we have seen fish living for months in an undiluted effluent. The "necessity for hurried disposal of wet sludges at any cost" exists only in cases of lime processes, and is not common to sludges obtained by neutral or acid processes, which are not an "intolerable nuisance," and which,—it would be invidious to mention names—so far from "begging for customers," find a ready sale at good prices.

The weakest point of the "Amines" process is the lime-character of its manure. No sensible farmer or gardener applies lime to his land in conjunction with farm-yard manure, night soil, ammonium salts, or other nitrogenous matter, as, in the long run, even calcium carbonate expels the nitrogen in the form of ammonia.

The strongest point of the "Amines" process is its economy. The lime process has been able to maintain its ground in virtue of its being cheap—and nasty; and if this new invention does away with the nastiness without sensibly affecting the cheapness it has doubtless before it no small future.

We learn that the Wollheim Syndicate has bought up or leased the patent-rights of S. Walter.

A QUICK METHOD OF PREPARING SILICON, ALUMINIUM, AND OTHER CHLORIDES IN QUANTITY.

By H. N. WARREN, Research Analyst.

The usual method resorted to for the preparation of anhydrous chlorides of those elements which are not themselves usually available, but obtainable rather as oxides is, as is well known, based upon the thorough mixing o the same with a sufficiency of carbon to replace the oxygen present, enclosing the same in a suitable enclosure consisting of either clay, or, more generally, glass combustion tubing, raising the same to an elevated temperature, and exposing the same to the action of chlorine gas. This, however, has, as regards a process, considerable drawbacks, both on account of the bulk of the mixture and the high temperature that is frequently required before decomposition of the oxide is effected.

For the preparation of silicon chloride, a sample of silicon-eisen containing about 15 per cent silicon was selected, introduced into a deep clay retort provided with a tubulure, and connected with an apparatus evolving dry chlorine gas, the pipe conveying the gas passing nearly to the bottom of the retort, while the stem of the same was connected to a suitable adapter, maintained at the required heat by the aid of hot water, and intended to condense or retain the volatile ferric chloride which would naturally accompany the silicon chloride, the end, or termination of the adapter being further connected with a suitable refrigerator containing a mixture of salt and ice in order to collect the volatile tetrachloride of silicon, $SiCl_4$.

The retort and its contents being now raised to redness by the aid of ignited charcoal, and the chlorine thus allowed to play into the same, almost immediately the dense greenish yellow vapour of gaseous ferric chloride is observed traversing the space within the adapter, and speedily condensing into the form of brilliant plates upon the walls of the same, while, at the more remote end, is observed the condensation of the silicon chloride, not unfrequently contaminated by the presence of small quantities of ferric chloride, which may, however, be entirely removed by subjecting the latter to distillation.

Further advantages may be obtained by substituting for the chlorine gaseous hydric chloride. This gas, on account of its forming with the iron a ferrous salt practically non-volatile at ordinary temperatures, is itself retained in the retort, and, at the termination of the reaction, may be detached by pouring the same while in the liquid form, while, at the same time, a further charge may be introduced. Thus, by acting upon the element silicon at an elevated temperature by means of gaseous hydric chloride a still more volatile liquid chloride of silicon is obtainable, corresponding to a hydro-trichloride, and represented by the formula of $SiHCl_3$. In this instance, however, the formation of silicon itself, which in the elementary form is by no means easy as regards its preparation, is absolutely necessary; but, by substituting for the same a sample of silicon-eisen containing a rich percentage of silicon, the corresponding chloride may be as readily prepared as in the former instance.

For the preparation of aluminium chloride an alloy of iron and aluminium containing about 10 per cent of the latter was selected, and the chloride thus obtained purified by intimately mixing it with iron borings and distilling the same; or the pulverised regulus mixed with common salt previous to exposing it to the action of chlorine yields, as a sublimate, aluminium-sodium-chloride.

Silicon chlorides, as also the corresponding bromides and iodides, which may be formed by a process analogous —namely, the substitution of either bromine or iodine in place of chlorine—are, at present, of no commercial value, but a simpler process than that usually resorted to may possibly be of benefit to those requiring the same when pursuing organic research. Their complete volatilisation have also induced the performance of several experiments with a view of ascertaining whether the reaction obtained is attended with any practical value.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

NOTICES OF BOOKS.

Appendices to the Investigation on Capillary Analysis and its Various Applications, as also on the Ascent of Colours in Plants. ("Beilagen ueber Capillaranalyse und ihre verschiedenen Anwendungen sowie ueber das emporsteigen der Farbstoffe in den Pflanzen"). Reprinted from the *Transactions of the Imperial and Royal Technical Museum of Vienna*, New Series, vol., ii., 1888, Nos. 3 and 4, and vol. iii., Nos. 1, 2, 3, and 4. By Prof. Dr. F. Goppelsroeder. Mulhouse: Wenz and Peters.

These appendices are concerned, in the first place, with the demonstration of the several colouring-matters in the organs of plants by means of capillary analysis. Plants belonging to sixty-seven families have been carefully examined, in most cases in their roots, stems, leaves, buds, and flowers.

In a second series of experiments the material operated upon was the alcoholic extract of the roots of plants prepared in the complete absence of sunlight.

A third series is devoted to an examination of the changes which the alcoholic extracts of the different organs of plants undergo on the addition of ammonia, caustic potassa, hydrochloric and sulphuric acids.

An appendix to Chapter II. gives an account of Schœnbein's original experiments on separations effected by means of capillary attraction.

A further appendix gives a reproduction of a memoir by Dr. F. F. Runge, which appeared as early as 1855, and

bears the title, "The Formative Impulse of Substances represented in Autogenous Pictures." Runge's original treatise is rare, if procurable; the abridgment here given will be interesting to all who wish to comprehend the possible effects of capillarity.

The Industry of Colours ("Die Farben Industrie"): A Quarterly Report on Results in the Region of Coal-tar, in the Chemistry of the Aromatic Compounds, of Artificial Colours, of Dyeing, Bleaching, Tissue Printing and Finishing. By E. Börnstein. Part 1st, October—December, 1888. Berlin: Mayer and Müller.

This new quarterly journal is a proof of the growing importance of that department of chemistry which concerns itself with the production and the application of colouring-matters. Various journals, English, French, and German, which devote themselves to subjects of this kind have certainly not been wanting, but the "Report" now before us possesses the advantage of presenting a complete view of all that has been done in this department during the past three months. To the many chemists and industrialists who have not time to search through an extensive series of journals and transactions this "Report" will prove a great convenience.

The arrangement here adopted is the following:—Coal-tar; the aromatic compounds, viewed in general, physically, physiologically, and theoretically; the benzol- and diphenyl-groups; the phenilised fatty hydrocarbons; the indol-, quinoline-, naphthaline-, phenanthene-, and anthracene-groups.

The third section treats of mordants and colours, and the fourth of bleaching, dyeing, printing, and finishing.

Chromelectro-Chemical Communications ("Farbelectrochemische Mittheilungen"). By Prof. Dr. Friedrich Goppelsrœder. Mulhouse: Wenz and Peters.

The author of this interesting pamphlet has been for some years engaged with the task of generating colouring-matters by the electrolysis of neutral, acid, or alkaline solutions of various salts of aniline, of the toluidines and their homologues, and also of the naphthylamine salts, phenol, &c. Not merely has he obtained in this matter colouring-matters, *e.g.*, alizarin, but he has succeeded in their electro-chemical fixation upon tissues. Specimens of this novel and interesting development of tissue-printing were exhibited by the author at the Manchester Jubilee Exhibition, in 1887. Thus, designs in aniline-black have been produced upon white, turkey-red, and vat-blue cotton-cloth, as also upon paper and parchment-paper.

One pattern shows the conversion of turkey-red into alizarin orange by the electrolysis of a solution of potassium nitrate. In another there is a white discharge on turkey-red produced by the electrolysis of ammonium chloride.

Many of the curious results here described cannot be made intelligible without reproductions of the accompanying illustrations. It seems to us, however, that Dr. Goppelsrœder's process, or rather processes, carry in them the germs of much that is likely to be of no small value—perhaps of a reorganisation of no small portion of the tinctorial arts. The author says, indeed, "The future must solve the question whether cylinders or plates acting as electrodes, plane or engraved, can find practical application, whether for the production of self-coloured grounds, or for the production of white or coloured designs upon coloured or white ground, discharges upon vat-blues, turkey-reds, &c., or other electro-chemical effects. The idea, however, of seeing a colour produced and in the same moment fixed upon the fibre has something supremely attractive for every chemist who appreciates Prof. Goppelsrœder's motto: "*Scientia vivat, crescat, floreat.*" Hence we can only hope that no unforseen economical difficulty may interfere.

On Capillary Analysis and its various Applications, as well as on the Ascent of Colouring Matters in Plants. By Professor Dr. Friedrich Goppelsrœder. Vienna: The author.

Capillary analysis is a method for the detection and separation of colouring-matters occurring in mixtures, by means of the varying speed with which they ascend in capillary tubes, *e.g.*, in unsized paper. The idea of utilising this phenomenon in the analysis of colouring-matters seems first to have occurred to the late Prof. Schœnbein, of Bâle, in or about 1861, and to have been elaborated by the author, who had been Schœnbein's pupil.

The method employed was substantially this:—Slips of pure filter-paper were suspended so as to dip for a few m.m. into the watery, alcoholic, ethereal, or other solutions of colouring matters. On withdrawal it was observed that if more than one colour was present they appeared in a series of successive strata. In this manner the impure coal-tar colours which were first introduced into commerce were easily resolved, qualitatively at least, into their constituents.

A similar method, depending likewise on capillary attraction, was described in an English work in 1870 (Slater, "Manual of Colours and Dye-wares"). The author states in his second edition that he "had used it privately, and shown it to friends since about 1860." But, however this may be, it is evident that the Schœnbein-Goppelsrœder method of applying the test is much more convenient than that of Slater, who merely placed a drop of the solution upon a piece of filter-paper, and observed whether the spot produced was homogeneous in colour, or spread out into zones of different colours. Goppelsrœder, after withdrawing his slips of paper from the solution, lets them dry, cuts off the parts which display different colours, dissolves each of them out by means of suitable solvent, and, if necessary, submits each solution separately to capillary analysis until perfectly pure colours are obtained.

Dr. Goppelsrœder next describes the application of capillary analysis in the detection of organic substances. In some cases minute traces may be detected in this manner.

In a following section we find this method applied in organic, and especially in tinctorial chemistry. The author points out that in recent coal-tar colours the traces of foreign matters are exceedingly slight in comparison with those observed a few years back.

Dr. Gopplesrœder considers that as far as colouring-matters are concerned, the capillary method is an excellent complement to absorption spectroscopy.

Capillary analysis, the author holds, will also prove of great importance in hygienic and forensic chemistry, in the detection of adulterated wines and beers, and pathological analysis.

This treatise, in short, must be recommended to almost every class of chemist. There are, we believe, few who will not find here useful hints, perhaps clues to new spheres of research.

CORRESPONDENCE.

THE TITRATION OF FERRIC SALTS.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 93), which has only just come under my notice, Mr. Clemens Jones contributes a paper on the titration of ferric salt solutions, in which the following sentences occur:—

"D. J. Carnegie (Chem. News, lvii., No. 1481) says that ferric solutions are instantaneously reduced by the use of zinc-dust. But there are obvious objections to its employment in quantitative work."

The obvious objections are not, however, stated.

If Mr. Clemens Jones had referred to the Chemical Society's *Journal* (*Trans.*, 1888), where my paper appeared *in extenso*, he would have found that the quantitative method described in connection with the reduction by zinc-dust gives very good results indeed, being in fact practically identical in principle with the one he himself advocates, viz., momentary contact of *slightly* acidified ferric salt solutions with finely divided zinc, followed by filtration from the excess of zinc prior to titration. As regards the filtration, the two methods differ, but the reversed filtration which I suggested is very simple and, I feel convinced, quite as effective as the method described by Mr. Clemens Jones, which involves such large and costly apparatus.

Zinc-dust is much more readily obtainable than pulverised zinc, and is generally so free from reducing impurity that the amounts employed in ordinary titrations do not introduce appreciable errors.—I am, &c.,

DOUGLAS J. CARNEGIE.

Gonville and Caius College, Cambridge.

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—The correct spelling is undoubtedly "vermilion." The word is so given in Ogilvie's "Imperial Dictionary," 1883; also in Buchanan's "Dictionary of Science and Technical Terms," 1876. I have no other works of general reference easily accessible, but the first-named dictionary should be sufficient authority. The Italian *vermiglio*, and French *vermeil*, from the Latin *vermiculus*, are equivalents.—I am, &c.,

EDWY GODWIN CLAYTON.

Chemical Laboratory,
43 and 44, Holborn Viaduct, E.C.,
September 11, 1889.

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—The French equivalent for ver-mil-ion is vermillon, and we have substituted an *i* for an *l* to produce something akin to the *y* sound of the double French *l*. If we use two *l*'s we spoil this effect, thus: ver-mil-lion. There appears, therefore, to be no doubt but that the correct way to spell vermilion is with one *l*. In those cases where two *l*'s are used they may be looked upon as slips of the pen caused by our familiarity with *million*. Mr. White is not very happy in his reasoning, that it should be spelt with one *l* because *vermeil* has only one; what about the feminine, *vermeille*? Besides, we might just as well argue that the correct way to spell battle is "batlle," because it is derived from or allied to *bataille*.—I am, &c.,

J. G. MCINTOSH,
Lecturer on Oils, Colours, and Varnishes,
Polytechnic Institute.

Service Chemistry. — An important volume, freely illustrated, entitled "Service Chemistry," will be issued immediately by Messrs. W. B. Whittingham and Co. It is a work upon which Professor Vivian B. Lewes, Lecturer at the Royal Naval College, has been laboriously engaged for the past year, with a view to bringing the entire subject up to the latest date. Chemistry, as affecting not only the Navy and the Army, but also the Merchant Service, is treated with technical detail.

The Use of Water-Gas.— MM. J. Lunge, O. Wyss, and M. Rothenbach (*Zeits. Angew. Chemie*).—The high proportion in water-gas of carbon monoxide necessitates special precautions. In the state of Massachusetts a lighting-gas may not contain at the outside more than 10 per cent carbon monoxide. For communicating to water-gas such an odour that an escape may be at once recognised the authors propose the addition of mercaptan. Further experiments are needed to decide whether this odour may not be lost in traversing the mains.

SCHOOLS OF CHEMISTRY.

THE following information was received too late for insertion in our Students' Number:—

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The Courses of Lectures, &c., are given in the various Buildings as follow:—

ANDERSONIAN BUILDINGS, 204, GEORGE STREET.

Professor of Chemistry.—William Dittmar, LL.D., F.R.SS. Lond. and Edin.

Chief Assistants.—James Robson and William Cullen.

Two Courses of Experimental Lectures on Chemistry: Daily from 10 to 11.—Junior, on Tuesdays and Thursdays; Senior, on Mondays, Wednesdays, and Fridays. The Lectures up to the end of the year are devoted to an Elementary Exposition of the Philosophy and the Methods of the Science, as illustrated by the History of the Non-metallic Elements. The rest of the Session is divided between the Chemistry of the Metals and Organic Chemistry, select chapters. In addition to occasional extemporised examinations during class hours, five written examinations are held during the Session, on Saturdays from 10 to 12. Fee, £2 2s.

The Laboratory is open daily (Saturdays excepted) from 10 to 4. Advanced students may obtain permission to work privately on Saturdays also until 1 p.m. The teaching is conducted on the tutorial system, each student working by himself, at a separate place, and on his own subject. Hence students of any grade of advancement may enter at any time, and the course of instruction can be adapted to the special requirements of the individual. Original research is not forgotten, but the Professor makes it a strict rule not to use his students as his private assistants in connection with his own investigations, and rather to discourage original research with students who have not yet obtained a sufficient mastery of all the practically important methods of chemical analysis and of preparative chemistry. Fee per month, £2 2s.; due in advance. For any period of six months or more, if paid in advance, at the rate of £1 15s. per month. The fees include the use of all the ordinary reagents, and of the resources of the laboratory generally; but the student has to find his own small apparatus (test-tubes, beakers, &c.), and also a few of the more expensive reagents—*e.g.*, chloride of platinum, nitrate of silver, molybdate of ammonia.

Supplementary Courses of Lectures and Laboratory Instruction are also given by the Assistants under the superintendence of the Professor.

An Evening Course of Lectures on the Fermentation Industries will be delivered by the Professor on Fridays from 8 to 9 o'clock, commencing on 18th October.

THE "YOUNG" CHAIR OF TECHNICAL CHEMISTRY, YOUNG LABORATORY BUILDINGS, 60, JOHN STREET.

Professor.—Edmund J. Mills, D.Sc. (Lond.), F.R.S.

Assistant.—Mr. William Baird.

This Chair has for its object the instruction of Students in Chemistry as applied to the various branches of industry in Chemical and other works.

LECTURES.—I. *Principal Course.*—A Course of Twenty-four Lectures will be delivered on Mondays, at 3 p.m., commencing on October 7th. These Lectures will refer mainly to the application of higher Chemistry, and are more especially intended for manufacturers, inventors, chemical engineers, and senior chemical students. Fee for the Course, One Guinea.

II. *Chemical Engineering.*—A Course of Twenty-four Lectures will be delivered on Tuesdays, at 3 p.m., commencing on October 8th. These will deal mainly with the construction and use of chemical plant.

III. *Technical Organic Chemistry*—A Course of Twenty-one Lectures will be delivered on Wednesdays at 2.30 p.m.,

commencing on October 9th. This Course is more particularly intended for Dyers, Colour Manufacturers, Brewers and Distillers, Tar Rectifiers, Drysalters, and others interested in a knowledge of Technical *Organic* Chemistry. Fee for the Course, £1 1s.

Evening Courses.—There will be a special evening course of twenty-four lectures on Photography, commencing on October 1st. These Lectures will be illustrated, and will be mainly of a practical character.

Laboratories.—The Laboratories are open daily from 10 to 4, and on Saturday from 10 to 1 o'clock for practical working by the Students, under the superintendence of the Professor and his Assistants.

The Fee for attending the Laboratories is £20 per Session of Nine Months, £14 10s. for Six Months, £7 10s. for Three Months, or £2 10s. per month.

Photographic Department.—The Laboratory contains a dark room provided with suitable appliances for copying, enlarging, and reducing, as well as for field work. Provision will be made to place at the disposal of Students a course of instruction in Photography sufficient to qualify them for Engineering, Calico-printing, and other works. Fee, the same as for Laboratory work.

Inventors, Patentees, and others whose investigations require isolation and privacy, as well as professional advice, can have Private Laboratories placed at their disposal. Electric Cable has been laid to these laboratories for the supply, if required, of adequate power.

Agricultural Chemistry.—Mr. C. M. Aikman, M.A., B.Sc., &c., will give courses of Evening Lectures on this subject. Elementary, Tuesdays, at 7. Senior, Fridays, 7 to 9.

Further information may be obtained of the Professor, at the Young Laboratory, 60, John St., Glasgow.

SCIENCE AND ART BUILDINGS, 38, BATH STREET.

Metallurgy and Mineralogy.—Professor, A. Humboldt Sexton, F.R.S.E., &c. Assistants: J. Morrow Campbell, B.Sc., and R. Law.

A course of lectures on Metallurgy on Mondays, Wednesdays, and Fridays, at 4 p.m., commencing on 7th October. Section I. on Mondays: Fuel and Refractory Materials. Section II. on Tuesdays: Manufacture of Iron and Steel. Section III.; Metallurgy of the Useful Metals other than Iron and Steel. Fee for any Section, £1 1s.; for the complete Course, £2 2s.

A Course of Lectures on Electro-Metallurgy will also be delivered on Wednesdays at 5.5 p.m. Fee, £1 1s.

The Metallurgical Laboratory is open daily from 10 to 4. Instruction is given in all branches of practical Metallurgy and Assaying. Fee, £2 2s. a month or £10 10s. for the session.

A course of instruction in Mineralogy, including the use of the blowpipe, &c., is given on Tuesdays and Thursdays from 4 to 5. Fee, £1 1s. Practical Course on Tuesdays from 2 to 4. Fee, £1 1s.

Evening classes in Chemistry, Metallurgy, and Mineralogy commence on Monday, September 30th.

ROYAL COLLEGE OF SCIENCE FOR IRELAND.

Professor.—W. N. Hartley, F.R.S., F.R.S.E., &c.

Assistant.—T. A. Shegog, F.C.S., F.I.C.

The instruction in chemical science embraces:—General Chemistry—A course of 60 experimental lectures on mineral and organic chemistry. About 15 tutorial classes are held by the Assistant Chemist. Applied Chemistry—(*a*) A course of 30 lectures on chemical manufactures; (*b*) A course of 30 lectures on metallurgy. Analytical Chemistry—A laboratory course of practical work, including qualitative analysis, quantitative analysis, assaying, and instruction in chemical research.

The college supplies, as far as practicable, a complete course of instruction in science applicable to the industrial arts, especially those which may be classed broadly under the heads of Mining, Engineering, and Manufactures, and is intended also to aid in the instruction of teachers for the local Schools of Science.

The Faculty of Manufactures was originally termed the Faculty of Chemistry, and the diploma of this Faculty is recognised by the Council of the Institute of Chemistry. By the kindness of manufacturers in Dublin the Professor has been able to conduct students of this Faculty through the chemical works of the district.

Students may also enter for the separate courses and receive certificates after examination. Certificates of attendance are granted to medical and other students, and such certificates are accepted by the Royal University of Ireland.

Further particulars may be obtained from the Secretary, Royal College of Science for Ireland, Stephen's Green, Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 8, August 19, 1889.

Remarks on the Conditions in which the Fixation of Nitrogen is Effected by Clayey Soils.—M. Berthelot.—The author states that since he reopened the question of the fixation of atmospheric nitrogen a number of eminent experimentalists have obtained results similar to his own. The new doctrine of the fixation of nitrogen by the joint action of the soil and of living organisms may be considered as established.

New Researches on the Fixation of Nitrogen by Vegetable Mould. The Influence of Electricity.—M. Berthelot.—The gain of nitrogen effected under the influence of vegetation has always been greater with electrised tree-pots than with such as were not electrised, both under glass bells and in the open air, in spite of the inferiority caused by the inequality of illumination. The same conclusion was arrived at in experiments performed on bare soil, provided, indeed, with microbia, but free from any higher vegetation. These results taken collectively seem to render probable an especial action of electricity, which promotes the fixation of nitrogen both in the soil and in the course of vegetation.

On Phosphotungstic Acids.—E. Péchard.—The author has obtained four distinct acids containing, to 1 equiv. of phosphoric acid, 6, 5, 4, and 3 equivs. of metatungstic acid.

Chemical and Thermic Study of the Phenolsulphuric Acids. Orthophenolsulphuric Acid.—J. Allain-le-Canu.—This is essentially a thermo-chemical paper, and as such it does not admit of useful abstraction.

The Combustion-Heat of Certain Organic Compounds.—S. Ossipoff.—The substances experimented upon are teraconic acid, maleic anhydride, methyl fumarate, and methyl maleate.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Newcastle-upon-Tyne Meeting of the British Association:—

President.—Sir I. Lowthian Bell, Bart., D.C.L., F.R.S., F.C.S.

Vice-Presidents.—Sir F. A. Abel, D.C.L., F.R.S.; Professor P. P. Bedson, D.Sc.; J. H. Gladstone, Ph.D., F.R.S.; Professor F. R. Japp, M.A., LL.D., F.R.S.; Professor G. D. Liveing, M.A., F.R.S.; Professor H.

M'Leod, F.R.S.; Professor J. Emerson Reynolds, M.A., F.R.S.; W. J. Russell, Ph.D., F.R.S.; Dr. E. Schunck, F.R.S.; Professor W. A. Tilden, D.Sc., F.R.S.

Secretaries.—H. Forster Morley, M.A., D.Sc. (Recorder); D. H. Nagel, M.A.; W. W. J. Nicol, M.A., D.Sc.; H. L. Pattinson, Jun.

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The Papers brought before the Section were as follows:—

President's Address.

Report of the Committee on the Influence of Silicon on the Properties of Steel.

Report of the Committee on the best Method of Establishing an International Standard for the Analysis of Iron and Steel.

Professor Liveing.—On Eikonogen, a new Photographic Developer.

J. W. Hogg.—The Volatilisation of Lead Oxide and its Action on Glass, at Low Temperatures.

C. T. Heycock, M.A., and F. H. Neville, M.A.—On the Molecular Weight of Metals: an application of Raoult's Method to Alloys.

Dr. J. B. Readman.—The Manufacture of Prussiate of Potash.

Report of the Committee for the purpose of Inquiring into and Reporting on the present Methods adopted for Teaching Chemistry.

Prof. P. P. Bedson, D.Sc.—On the Manufacture of Aluminium from Cryolite.

J. Pattinson and Dr. H. S. Pattinson.—On Chilian Manganese Ore.

Professor Frank Clowes, D.Sc.—On Barium Sulphate Deposits from the Waters of Durham Coal-mines and in Nottingham Sandstone.

J. H. J. Dagger, F.I.C.—The Manufacture of the Alloys of Aluminium in the Electric Furnace.

Report of the Committee on the Bibliography of Solution.

Report of the Committee on the Properties of Solutions.

Report of the Committee on the Absorption Spectra of Pure Compounds.

Report of the Commit.ee on the Action of Light on the Hydracids.

Report of the Committee on the Silent Discharge in Oxygen.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. Arthur Richardson.—A new form of Self-registering Actinometer.

Professor H. B. Dixon, F.R.S.—Explosion of a Mixture of Hydrogen, Chlorine, and Oxygen.

Professor H. B. Dixon, F.R.S., and J. A. Harker.—On the action of Light on dry Hydrogen and Chlorine.

Dr. A. P. Laurie.—On Artists' Colours.

Dr. William Newton.—Specific and Latent Heats in Relation to the Combining Heats of the Elements.

Dr. A. Scott.—Composition of Water by Volume.

P. Braham.—A Spectroscope without a Lens.

Discussion on Blast Furnace Practice.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on the Formation of a Uniform System of Recording the Results of Water Analysis.

Professor Percy F. Frankland, Grace C. Frankland, and J. J. Fox.—Contributions to the Study of Pure Fermentation.

S. A. Sworn, B.A.—The Constitution of the Aromatic Nucleus.

S. A Sworn, B.A.—The Reaction of Benzoquinone with Potassium Cyanide.

J. B. Hannay.—A new White Lead.

Dr. Issac Ashe.—Dimidium: an attempt to Represent the Chemical Elements by Physical Forms.

P. J. Hartog, B.Sc.—Researches on Sulphites.

Dr. J. B. Cohen.—Metallic Aluminium as a Chemical Reagent.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Cement.—Can any reader refer me to papers on Portland cement, particularly those dealing with the chemistry of the subject, published here or on the Continent? I have Le Chatelier's work.—Cement.

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THE CHEMICAL NEWS.

Vol. LX. No. 1558.

ON EIKONOGEN, A NEW PHOTOGRAPHIC DEVELOPER.*

By Professor G. D. LIVEING, F.R.S.

This substance is the sodium salt of amido-β-naphthol-β-sulphonic acid.

The acid with this long name, $C_{10}H_5.NH_2.OH.SO_3H$, was first described by Professor Meldola in 1881. He obtained it by the reduction of nitroso-β-naphtholsulphonic acid (*Chem. Soc. Journ.*, xxxix., 47). It has since been obtained in much larger quantity by Witt, by reducing the orange colouring matter from diazo-benzene chloride and Schaeffer's β-naphthol sulphonic acid (*Annalen Ch. and Ph.*, 152, 298), and he described his process and the characters of the product in the *Proceedings of the German Chem. Society* last December.

It is now produced on the manufacturing scale by the *Actiengesellschaft fur Anilinfabrikation* at Berlin, and may be obtained in the markets, and I think it may be of interest to chemists as well as photographers.

Eikonogen crystallises well from solution in water, and the crystals contain two molecules of water of crystallisation. It dissolves with tolerable facility in hot water, but is only sparingly soluble in cold water, and is insoluble in alcohol. The aqueous solution quickly turns yellow, and gradually brown. An akaline solution turns brown immediately from absorption of oxygen. To keep the aqueous solution for any time it is necessary to add sodium sulphite. Even with the addition of sodium sulphite I have found that it does not remain colourless very long.

I need not say that a great variety of reducing agents may be used as photographic developers, but the most essential quality to secure is that the reducing agent shall quickly reduce those portions of the silver compound which have been exposed to light, but shall have no effect, or no rapid effect, on the silver compound which has not first been acted on by the light; in fact, that the reduction shall extend to the faintest lights, but shall never spread beyond the particles which have received the impulse of light. Of all substances tried, perhaps pyrogallol has held its own the longest, though some prefer ferrous oxalate, and of late hydroquinone has been a good deal used. The chemical action of hydroquinone is very similar to that of pyrogallol, and the fact that the former is paradihydroxybenzene, and pyrogallol is a trihydroxybenzene, led Dr. Andresen, of Berlin, to try the effect of other para-derivatives of benzene which, by oxidation, would easily give quinones or similar substances. Para-diamidobenzene and para-amidophenol were found to be well adapted for developing photographs. Subsequently Dr. Andresen turned his attention to the sulphonic acids, and the outcome has been that eikonogen appears to fulfil the requirements of a good developer the best.

Dr. Andresen claims for it—

1. That while eikonogen reduces the bromide of silver so far as it has been subject to the action of light, the bromide in dry gelatin plates which has not been exposed to light remains unaffected by it.

2. That concentrated solutions of eikonogen (1 : 20 to 1 : 50) produce even with instantaneously exposed plates minutely detailed negatives.

3. The minuteness of detail produced by eikonogen is supposed to be due to the fine grain of the silver precipitate.

4. The tone of the negatives given by eikonogen is well adapted for printing, and in this respect it excels pyrogallol.

5. The solutions of eikonogen containing sodium sulphite are durable even after the addition of carbonate of soda, and the same solution can be used for several pictures in succession.

6. Eikonogen is not poisonous, which cannot be said of pyrogallol or hydroquinone.

The specimens which I exhibit bear out, I think, the claims. The negatives are remarkably perfect in detail, the tone is excellent, blacker than is given by pyrogallol, more delicate than is given by ferrous oxalate, and the prints from them are very good. I need not say that they have been taken by an experienced photographer.

My own experience of eikonogen is, as yet, very limited, and my practice of photography is limited to spectroscopic photography and negatives. It is necessary for me to have a very sensitive developer, which will develop the faintest details and, at the same time, give all the shades of depth which correspond to variation in the brightness of the spectral lines. Hitherto I have not found anything do so well for my purpose as pyrogallol; but eikonogen seems as sensitive as pyrogallol, and at the same time to give me a picture in which the lines are blacker and more easily seen under a microscope. I cannot quite endorse Dr. Andresen's claim that solutions of eikonogen with sodium sulphite are very permanent. The same solution can, however, be used for several pictures in succession. For instantaneous photographs the solution has to be made alkaline with caustic alkali, and then the liquid becomes brown very quickly. For portraits, and such like pictures, an alkaline carbonate, such as sodium carbonate, may be used.

As regards the non-poisonous character of eikonogen, I suspect it can only be due to its sparing solubility, for so powerful a reducing agent can hardly fail to have a strong effect on the animal economy.

* Read before the British Association, Section B, Newcastle Meeting.

ACETYL DERIVATIVES OF CELLULOSE.

By C. F. CROSS and E. J. BEVAN

In recent numbers of the *Berl. Berichte* (1889, 1464 and 2207) Erwig and Kœnigs describe the preparation of a pentacetyl dextrose by the method proposed by A. P. N. Franchimont in 1879 (*Ber.*, xii., 2059), which consists in adding zinc chloride to the anhydride in place of sodium acetate (Liebermann) as the auxiliary.

The acetylation of cellulose by this method was studied by Franchimont, who found that the main product was the triacetyl derivative. The last communication by this author on the subject (*Compt. Rend.*, xcii., 1053) promises a further investigation. Some years have, however, elapsed, and, the matter not having been further advanced, we have thought it expedient to reopen the subject. The method we have followed is as follows:—

The anhydride is heated to the boiling-point, a fragment of zinc chloride dissolved, and the cellulose—specially purified cotton-wool—added in successive small portions. The digestion was continued two to three days. Preliminary observations on the crude product of the reaction, separated on treatment of the filtered solution with water, showed that the acetic acid obtained by saponification was considerably in excess of the quantity obtainable from triacetyl cellulose.

The product was purified by solution in glacial acetic acid, the solution being limpid and not gelatinous as stated by Franchimont in the case of triacetyl cellulose, and filtering. The filtered solution was divided into two parts, one of which was treated with water directly, the precipitated product being washed and dried (*a*); to the other permanganate solution was added in successive small portions, and then water in excess. The flocculent

precipitate was treated with sulphurous acid, finally washed, and dried (*b*). The products—(*a*) crude and (*b*) purified—were analysed, with the following results:—

	(*a*).	(*b*).
C	52·3	51·6
H	5·6	5·8

The carbon percentage calculated for the triacetyl derivative is 50·0, for pentacetyl cellulose 51·6. More conclusive, however, than these numbers are those afforded by the determinations of the acetic acid yielded on saponifying the product. These varied from 79 to 82 per cent with various preparations. The percentages calculated for the tri-, tetra-, and pentacetyl derivatives are respectively 62, 73, and 81. As the evidence stands at present, therefore, the soluble product of the original reaction appears to be a pentacetyl cellulose.

The formation of such a derivative would of course have a very important bearing on the question of the constitution of cellulose, and we therefore reserve any more positive statements as to its composition than are contained in this bare record of experimental results. The results of our continued investigation will form the subject of a fuller communication at an early date.

4, New Court, London, W.C.,
September 19, 1889.

NOTE ON DIFFUSION.

By W. A. DIXON, F.I.C., F.C.S.,
Lecturer on Chemistry, Sydney Technical College.

From all text-books put into students' hands they come to very erroneous conclusions on the subject of diffusion, as I have found by experience both in teaching and examining during many years. I am induced to send this note, as I find the usual form of statement in the beginning of Prof. Mendeleeff's lecture in Chemical News, vol. lx., p. 1, just to hand, when he says:—"The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air"; and lower down he speaks of diffusion through colloidal substances.

This is, of course, quite correct, but students and those ignorant of the subject always infer that the diaphragm, porous in the case of gases or colloidal in the case of liquids, is *the* point of importance, when actually they have no more to do with diffusion than the diaphragm in the body of a microscope has to do with the magnifying power of the objective.

In text-books usually the first example of diffusion given and illustrated is a vessel of chlorine attached by a tube to a vessel of hydrogen, the latter being uppermost, showing that in a certain time the gases become uniformly mixed against the action of gravity. Students are not told, however, that in this experiment two different actions go to produce the effect. Roughly speaking, the diffusive action of the hydrogen is about six times that of the chlorine; so when six volumes of the former pass into the space occupied by the latter, of which one volume only diffuses, the result is an increase of pressure in the lower vessel and a decrease in the upper. The vessels being in free communication, the pressure is instantly adjusted by a flow of mixed gases from the lower to the upper as a current. This being explained, the action of a diaphragm comes simply into play as preventing the passage of the current without interfering with the diffusive action, and Graham's molecular sieve is at once understood. The diaphragm cuts off current in either liquid or gaseous diffusion as the microscope diaphragm cuts off aberration.

In connection with this the statement is often made that, a vessel being filled with one gas, another gas introduced occupies the whole space as if it were a vacuum, without one word about increase of pressure or volume, which leads to some curious misconceptions on the part of even well-educated intelligent people.

CLASSIFICATION OF THE ATOMIC WEIGHTS IN TWO ASCENDING SERIES, CORRESPONDING TO THE GROUPS OF ARTIADS AND PERISSADS.*

By W. R. LIVERMORE, Major of Engineers, U.S. Army.

If the atomic weights of all chemical elements are arranged in a single ascending series, it will take the following form if expressed in whole numbers:—

1,—7, 9, 11, 12, 14, 16, 19,—23, 24, 27, 28, 31, 32, 35,—39, 40, 44, 48, 51, 52, 55, 56, 59, &c.;

corresponding to the elements,—

H,—Li, Be, B, C, N, O, F, —Na, Mg, Al, Si, P, S, Cl,—K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, &c.

The well-known "Law of Octaves" calls attention to the fact that each element bears a strong resemblance to that seven places from it in this series, and the "Periodic Law" states that the properties of elements stand in periodic relation to their atomic weights. These laws have been enunciated and illustrated by Newlands, Mendeleeff, Lothar Meyer, and others, and are now familiar to all students of chemistry.

Referring to these laws, Wurtz, in his "Atomic Theory," says:—"Though it may be generally true that the properties of bodies are subject to periodic modifications with the increase of their atomic weights, the law of these modifications escapes our observation, and seems to be of a complicated nature; for on the one hand, the atomic weights of successive elements vary within considerable limits without displaying any regularity in these variations; on the other hand, we must confess that the gradations of properties—in other words, the greater or less divergences between properties of successive elements—do not appear to depend upon the degree of the differences between the atomic weights. These are real difficulties."†

Lothar Meyer on the same general subject says:—"There can be no doubt as to the fact that these differences are subject to law";‡ and, "There is still much work for the hands and mind; but it will be thoroughly rewarded. The prize is a systematic inorganic chemistry which will bear comparison with the thoroughly developed system of organic chemistry."§

The object of this paper is to contribute to the removal of these difficulties, by showing that the increase in the atomic weights of the elements follows a law of the utmost simplicity in its general form, and identical with that of the series of organic compounds.

Let us take the series above mentioned and consider whether any of its terms can be classed in a series of constant increase. Beginning with 2 as a modulus, we find that it applies to 7, 9, and 11, with no recurrence of this difference except for the terms 12, 14, 16; 3 applies only to 9, 12,—24, 27,—48, 51, and to 16, 19 * * 28, 31 * * * * * 52, 55; 4, however, applies to 7, 11 * 19, 23, 27, 31, 35, 39 * * 51, 55, 59, and to 12, 16 * 24, 28, 32 * 40, 44, 48, 52, 56; thus embracing in two parallel series all the terms of the first three periods of Newlands and Mendeleeff, with the exception of 9 and 14, *i.e.*, 22 out of 24. The probability that these numbers would so far

* A Paper presented to the American Academy of Arts and Sciences April 10, 1889.
† "The Atomic Theory," 1881, p. 162.
‡ "Modern Theories of Chemistry," English Translation, 1888, p. 160.
§ *Ibid.*, p. 170.

coincide with the regular series from the result of chance is too slight to be entertained. If now, in addition to this coincidence, any points of resemblance can be discovered among several of the elements in each series, such resemblances are significant; but when it appears that all, or nearly all, in each series fall into a distinct group that has already been recognised as such by chemists, there is scarcely room for doubt that the regularity of the series is connected with the intrinsic nature of the elements.

Those of the first series are all perissads, and those of the second artiads, or elements of uneven and even quantivalence respectively, with the single exception in one case of scandium, a newly discovered element whose atomic weight has never been so accurately determined as to throw it out of its group, and cobalt and nickel, which apparently belong to another group. For the present, therefore, the law of regular increase in the atomic weight of the parallel series is spoken of as the law of artiad and perissad increase, or more briefly as the Perissad Law.

By similar methods, we find that the numbers between 70 and 100 fall naturally into two series, with the common difference of 5 for the perissads and perhaps 4 for the artiads. The latter series, however, is somewhat indefinite.

Between 100 and 150 the perissads increase regularly, with a common difference of about 6½, and the artiads less regularly, with the same difference, as shown in Tables I. and II.

Too little is known of the atomic weights between 150 and 190, and of those above 210, to justify their classification. Between 190 and 210 we find that 4 applies to 195, 199 * 207, and to 196, 200, 204, 208.

All of the first series are artiads, and in the second all except 200, or Hg, are recognised as perissads, and this element is so similar in many respects to Cu, Ag, and Au that for the present it is allowed to remain in its place. There only remain unclassified, 9, 14, 59, 104, and 193. Of these numbers, 9 is the atomic weight of Be and appears to differ too much from 8, the serial number of this element, to be recognised in its natural place.

The remaining numbers, 14, 59, 104 * 193, form a series by themselves, with a difference of a little less than 45. Ni and Co correspond to 59, Ru and Rh to 104, and Ir to 193. These elements are always classified together, and this regularity of increase has often been noticed. But perhaps 14 or N falls into this series accidentally.

In Tables I. and II. the first column shows the symbols for the elements; the second column, the serial numbers derived from the formula; the third column, the observed atomic weights; and the fourth column, the deviations from the serial numbers. The next columns show the specific gravity, the atomic volume, the fusibility, malleability, and place in an electro-chemical series for each element, and the last column, the group in the classification of Newlands and Mendeleeff to which the element has been assigned. The horizontal lines divide the series and periods of this system.

The observed atomic weights are taken from the lists of Clarke,* L. Meyer,† and Van der Plaats,‡ and in most cases by selecting for each element that one of the values that differs least from the mean, taking oxygen at 16 for a standard, and expressing but one place of decimal fractions. The data for the next four columns are taken from Meyer's "Modern Theories." To express their fusibility, the elements are divided into seven classes, that represented by 1 being the most fusible. The brittle and malleable elements are distinguished by the initial letters B and M. In the electro-chemical series, taken from Barker's "Text-book of Chemistry,"§ 1 is the most electro-positive in an acid solution, and 63 the most negative.

It appears from these tables that none of the deviations from the serial numbers exceed 0·6 excepting that for Cb among the perissads, and Zn and Mo among the artiads; Zn differs by just a unit, and seems to form an exception to the regularity.

In his account of the Discovery of the Periodic Law,* Newlands points out the irregularity of the single series, illustrating it by several tables, and the data are clearly set forth and tabulated in a recent paper by Venable, on the "Re-calculation of the Atomic Weights."†

In the artiad grand group no atomic weight corresponds to 20, 36, 83, or 131, and a reference to the electro-chemical series will show that these are the points at which the elements change from a negative to a positive maximum, corresponding also to the maximum atomic volumes, and to the end of the Mendeleeff periods.

These points are marked with asterisks in the table.

Analogy points to the possibility of elements with atomic weights of 15, 43, or 44, 47, 60, and perhaps of 99, 100, and 143·5.

The newly discovered philippium and praseodymium may perhaps correspond to 47 and 143·5, respectively, but there appears to be no place in either series for neodymium, or 140·3.

TABLE I.—*Perissads.*

El.	Atomic Weights. Ser.	Obs.	Dev.	Physical Properties. Sp. gr.	At. vol.	Fus.	Mal.	Elec:	Gr.
H	1	1·0	0·0	—	—	—	—	—	I.
	+ 6 + *n* × 4								
Li	7	7·0	0·0	0·59	11·9	1	M	5	I.
B	11	11·0	0·0	2·68	4·0	6	B	49	III.
	15	?							
F	19	19·0	0·0	—	—	1	B	60	VII.
Na	23	23·1	+0·1	0·97	23·7	1	M	4	I.
Al	27	27·1	+0·1	2·56	10·6	3	M	13	III.
P	31	31·0	0·0	2·30	13·5	2	B	55	V.
Cl	35	35·5	+0·5	1·38	25·6	1	B	59	VII.
K	39	39·1	+0·1	0·86	45·4	1	M	3	I.
Sc	43	44·?	—	—	—	—	—	—	III.
	47	?							
V	51	51·3	+0·3	5·50	9·3	7	B	52	V.
Mn	55	55·0	0·0	8·00	6·9	5	B	19	VII.
Co?	59	(59·0	0·0	8·50	6·9	5	M	23)	
Cu	63	63·5	+0·5	8·80	7·2	3	M	31	I.
	+ 7 + *n* × 5								
Ga	70·0	70·0	0·0	5·96	11·7	1	?	?	III.
As	75·0	75·0	0·0	5·67	13·2	2	B	54	V.
Br	80·0	80·0	0·0	2·97	26·9	1	B	58	VII.
Rb	85·0	85·4	+0·4	1·52	56·1	1	M	2	I.
Y	90·0	89·8	−0·2	—	—	—	—	11	III.
Cb	95·0	94·2	−0·8	6·27	15·0	7	B	44	V.
	100·0								
	+ 7·5 + *n* × 6·25								
Ag	107·5	107·9	+0·4	10·50	10·2	3	M	32	I.
In	113·7	113·7	0·0	7·43	15·3	1	M	27	III.
Sb	120·0	120·1	+0·1	6·70	17·9	2	B	47	V.
I	126·3	126·8	+0·5	4·94	25·6	1	B	57	VII.
Cs	132·5	132·9	+0·3	1·88	70·6	1	M	1	I.
La	138·8	138·8	0·0	6·20	22·3	3?	—	18	III.
Di	145·0	145·0	0·0	6·50	22·3	3?	—	17	V.
	? + *n* × 4								
Au	196·0	196·6	+0·6	19·30	10·2	3	M	40	I.
Hg	200·0	200·2	+0·2	13·59	14·7	1	M	33	II.
Tl	204·0	204·2	+0·2	11·86	18·1	2	M	24	III.
Bi	208·0	208·0	0·0	9·82	21·1	2	B	29	V.

* "The Constants of Nature." "A Re-calculation of Atomi Weights," 1882.
† "Modern Theories of Chemistry," English Translation, 1888.
‡ "Verification of the Atomic Weights of M. Stas."
§ "Text-book of Chemistry," p. 16.

* "The Periodic Law," p. 27.
† *Journal of Analytical Chemistry*, January, 1889, p. 48.

TABLE II.—*Artiads.*

El.	Atomic weights. Ser.	Obs.	Dev.	Physical Properties. Sp. gr.	At. vol.	Fus.	Mal.	Elec.	Gr.
	$12 + n \times 4$								
		?							
C	12·0	12·0	0·0	0·33	3·6	7	B	54	IV.
O	16·0	16·0	0·0	—	—	1	B	63	VI.
	20·0	*							
Mg	24·0	24·0	0·0	1·74	13·8	3	M	9	II.
Si	28·0	28·1	+0·1	2·49	11·2	6	B	42	IV.
S	32·0	32·1	+0·1	2·04	15·7	1	B	62	VI.
	36·0	*							
Ca	40·0	40·0	0·0	1·57	25·4	2	M	8	II.
	44·0	?							
Ti	48·0	48·1	+0·1	—	—	—	B	43	IV.
Cr	52·0	52·3	+0·3	6·80	7·7	5	B	53	VI.
Fe	56·0	56·0	0·0	7·80	7·2	5	M	21	VIII.
	60·0	?							
Zn	64·0	65·0	+1·0	7·15	9·1	2	M	20	II.
	$+ 7 + n \times 4$								
Ge	71·0	?	—	?	—	?	—	?	IV.
As	75·0	75·0	0·0	5·67	13·2	2	B	54	V.
Se	79·0	79·0	+0·0	4·60	17·1	1	B	56	VI.
	83·0	*							
Sr	87·0	87·5	+0·5	2·50	34·9	2	M	7	II.
Zr	91·0	90·6	−0·4	4·15	21·7	6	B	14	IV.
Mo	95·0	95·9	+0·9	8·60	11·1	6	B	51	VI.
	99·0	?							
	$+ 7 + n \times 6{\cdot}25$								
Pd	106·0	106·0	0·0	11·50	9·2	4	M	34	VIII.
Cd	112·2	112·2	0·0	8·65	12·9	2	M	25	II.
Sn	118·5	118·0	+0·5	7·29	16·1	2	M	28	IV.
Te	124·8	125·0	−0·2	6·25	20·2	2	B	46	VI.
	131·0	*							
Ba	137·2	137·1	−0·1	3·75	36·5	2	M	6	II.
Ce?	143·5	?	?	6·70	21·0	3	? —	16	IV.
	$? + n \times 4$								
Pt	195·0	194·9	−0·1	21·50	9·1	5	M	37	VIII.
Os	199·0	198·9	−0·1	22·50	8·7	5	B	39	VIII.
	203·0	?							
Pb	207·0	206·9	−0·1	11·38	18·1	2	M	26	IV.
	$14 + n \times 44{\cdot}8$								
Ni	58·8	58·7	−0·1	8·80	6·7	4	M	22	VIII.
Co	58·8	59·0	+0·2	8·50	6·9	5	M	23	VIII.
Ru	103·6	104·0	+0·4	12·26	8·4	5	B	35	VIII.
Rh	103·6	104·2	+0·6	12·10	8·6	5	M	36	VIII.
	148·4	?							
Ir	193·2	193·0	−0·2	22·46	8·6	5	B	38	VIII.

In each of the grand groups, perissads and artiads, the breaks between the minor groups of common difference occur at, or near, the minimum points of the series of atomic volumes, and therefore midway between the dividing lines above mentioned.

The first term of each of the groups of common difference, except the first, viz., Ga, Ag, Au, Ge, Pd, and Pt, appears to be a heavy malleable metal, electrically neutral, and with an atomic volume a little above 9 in the artiad, and 10 in the perissad groups.

With the increase of atomic volume is generally associated an increase in electro-negative properties, and, as a rule, the elements become fusible, brittle, and diamagnetic.

With the maximum atomic volume, the elements change from the extreme of negative to positive, from diamagnetic to magnetic, from brittle to malleable; and with the decrease of volume they lose their electro-positive properties, and, as a rule, become at last brittle and infusible.

The study of the periodic law has directed attention to the relations between the atomic weights and these properties, many of which were previously treated as functions of the electro-chemical order.

When the exact atomic weights are all determined with sufficient accuracy, it is natural to infer that the deviations from the regular increase will show a law as significant as the approximate coincidence with the serial numbers, and even now we see clear evidences of this law. To make it more apparent, it will first be necessary so to adjust the formula as to reduce these differences to a minimum, and in the low atomic weights to take account of smaller fractions.

The formula $a + nd$ then has the following values for the several groups of common difference:—

$6{\cdot}99 + n \times 4{\cdot}02$	$12{\cdot}00 + n \times 4{\cdot}01$
$70{\cdot}25 + n \times 4{\cdot}85$	$74{\cdot}88 + n \times 4{\cdot}12$
$107{\cdot}85 + n \times 6{\cdot}20$	$105{\cdot}98 + n \times 6{\cdot}22$

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act, 1871.*

London, September 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Two samples, out of the 175 examined, manifested a "very slight turbidity." The remaining 173 samples were found to be clear, bright, and well filtered.

The improvement in the London Waters, to which we referred in our Report for last month, was well maintained during August. This is seen by comparing the oxygen required to oxidise the daily samples of the water as supplied by the several Companies:—

Oxygen (Per Gallon) Required to Oxidise the Organic Matter.

	July.	August.
New River Company	0·024	0·019
East London Water Company ..	0·045	0·036
Thames-derived Water Companies	0·040	0·037

These details by the oxygen process are fully corroborated by the estimations of the Organic Carbon and Nitrogen which are duly recorded in the tables.

The results generally of our daily examinations, show

the water as supplied by the several Companies to be entirely satisfactory.

We are, Sir,

Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

DETERMINATION OF CARBON IN THE IRONS OF COMMERCE.

By L. BLUM.

Under this title L. L. de Koninck recently published a communication recommending, before the combustion of the residual carbon with chromic acid and sulphuric acid, to introduce into the combustion-flask a little silver sulphate in order to convert any chlorine compounds which might have escaped removal by washing into insoluble silver chloride.

Koninck's assumption on which this proposal is based, *i.e.*, that the silver chloride formed is not attacked by the mixture of chromic and sulphuric acid, is in full contradiction to other authors. A. Sauer (*Zeitschrift Anal. Chemie*, vol. xii., p. 176) decidedly contradicts the assumption that silver chloride is scarcely, if at all, attacked by concentrated sulphuric acid. He observed that it is completely dissolved and decomposed, with the escape of hydrochloric acid. In an editorial note on Sauer's memoir we find it stated that, according to A. Vogel, boiling oil of vitriol slowly dissolves silver chloride, with escape of hydrochloric acid and formation of silver sulphate. According to Volhard (*Zeitschrift*, xviii., p. 281), sulphuric acid diluted with half its volume of water does not attack silver chloride. This, however, is a degree of dilution which never occurs in the combustion of the carbon in irons.

To arrive at certainty the author performed the following experiments:—

50 c.c. concentrated sulphuric acid were mixed with a drop of hydrochloric acid, well shaken up, and a drop of the solution of silver nitrate was then added. There appeared a white precipitate of silver chloride, which was completely dissolved on boiling. The liquid was set aside in the cold until the next day, but it remained clear. Testing for chlorine gave a negative result; the silver chloride had, therefore, been completely dissolved by boiling with concentrated sulphuric acid, with expulsion of hydrochloric acid.

The following experiment bears more directly upon the proposal of De Koninck:—

The combustion-flask of an apparatus for determining carbon in iron was charged with an unweighed quantity of silver chloride, about 10 grms. chromic acid, and 100 c.c. concentrated sulphuric acid. The silver chloride had been prepared by precipitating a few drops of hydrochloric acid with excess of silver sulphate, so that no chlorine was present except in combination with silver. The water used in rinsing the silver chlorine into the flask was about 20 c.c. In conducting the experiment all precautions were observed which are recommended for the determination of carbon by combustion with chromic acid and sulphuric acid. As a recipient was used a Geissler absorption apparatus filled with potassa-lye. It weighed—

After the experiment	68·3165 grms.
Before „	68·0670 „
Increase..	0·2495 „

Between the combustion-flask and a washing-bottle filled with concentrated sulphuric acid there was interposed a U-shaped bulb-tube as a refrigerator. In it there had been condensed during the operation a small quantity of water. On being acidulated with nitric acid and mixed with silver nitrate it weighed, after ignition, 0·0098 grm.

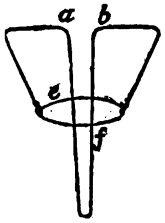
According to these experiments the proposal of De Koninck appears utterly useless.—*Zeitschrift f. Anal. Chemie* (Vol. xxviii., Part 4, pp. 450—452).

FILTERING ARRANGEMENT.

By C. R. GYZANDER,
Chemist, Cochrain Chemical Co., Boston, Mass., U.S.A.

A filter support, which is an improvement on the arrangement for rapid filtration described by Mr. R. A. Fessenden in the Chem. News, vol. lx., p. 102, is shown in accompanying sketch. It is made from platinum wire, copper wire, or any other suitable material, and bent in the shape shown in Fig 1.

Fig. 1.



A paper, folded as described by Mr. Fessenden, is pushed in between the wires *a* and *b*, Fig. 1, which serves the same purpose as the glass rod, that is to support the inner folds of the filter; whereas the ring *c f* supports the outer folds, giving the whole an appearance of a paper formed with two compartments. This may now be placed in a glass funnel, or used alone, simply by

Fig. 2.

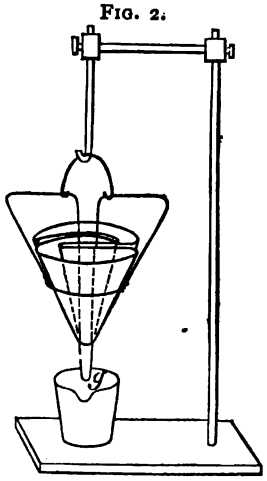
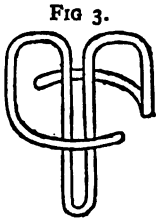


Fig 3.



suspending it over the beaker as in Fig. 2, the liquid following the wire and dripping from the point *g*.

As a means of drying precipitates on the filter, it is far superior to the old way of placing the glass found with its filter in the drying oven, as the air has access to the paper from all sides, whereby it dries much more rapidly and thoroughly. For a 7½-inch filter, a support of $\frac{1}{32}$-inch platinum wire, with the ring *c f*, 2½ inches in diameter, and the wires *a* and *b*, 3 inches long, gave excellent service. A glass rod bent as indicated by Fig. 3 works very well.

SODIUM NITROPRUSSIDE AS A REAGENT FOR CAUSTIC ALKALIES AND ALKALINE EARTHS.

By H. BRUNNER.

Whilst engaged in another investigation the author observed that sodium nitroprusside, if mixed with caustic soda or potassa, produces an intense yellow colouration. Baryta- or lime-water react in the same manner, whilst soluble carbonates and bicarbonates have no effect. Hence it appears that sodium nitroprusside is not merely a reagent for soluble metallic sulphides and sulphhydrates, but also for soluble metallic oxides and hydrates.

If an aqueous solution of sodium nitroprusside is mixed with sodium hydrate until an orange colour appears and alcohol is then added, after shaking and settling a deep yellow oil is separated out, which, on prolonged standing, solidifies into fine orange-coloured crystals. A watery solution of this sodium salt, the composition of which has not yet been determined by the author, gives coloured precipitates with metallic salts. The soda salt serves as a reagent for acids, with which its solution gives a green colour, which, on exposure to the air, turns violet, and finally gives a green precipitate.—*Schweitzer Wochen Pharmacie* and *Chemiker Zeitung*.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. Franz Hundeshagen.

The conditions of the formation of yellow phosphomolybdic acid and its complete separation as an ammonium salt, although of the highest analytical importance, are as yet but superficially known. The execution of Sonnenschein's process in its various applications and modifications is therefore often involved in difficulties, and often does not lead to an accurate result, especially when it is required to separate and determine very small quantities of phosphoric acid. It is, therefore, worth while to examine the causes which may have a disturbing effect in the precipitation of phosphoric acid by molybdic acid, and to establish methodically the conditions which lead to uniform and trustworthy results.

1. *Influence of the Nature of the Solution upon the Composition of the Precipitate.*

The author finds the composition of the precipitates obtained under the most varying conditions (if only free from free molybdic acid and other impurities), after washing with cold dilute nitric acid and drying at 130°—150°, to have in all cases the formula $12MoO_3.PO_4.(NH_4)_3$, whether the precipitation had been effected in strongly or slightly acid nitric, hydrochloric, or sulphuric solutions containing more or less ammoniacal salt, dilute or concentrate, hot or cold solutions; and whether phosphoric or molybdic acid was present in excess, or if the solution contained foreign salts (*e.g.*, potassa) or not.

The precipitate obtained with excess of acid, washed with cold dilute acid, and dried in the desiccator over calcium chloride and caustic potassa until the weight became constant, contained, according to the acid in the presence of which the precipitation ensued, and which served for washing two mols. NO_3, H, or ClH with one mol. H_2O, probably in an unstable chemical combination. Both acid and waterwere partially expelled at a moderate heat, but quickly and completely at temperatures exceeding 130°.

In determining the phosphoric acid and the molybdic acid, the author used the compound dried between 130° and 150°. The molybdenum was determined not as sulphide, but as MoO_3, as it was difficult to obtain a sulphide of constant composition. After the phosphoric acid had been separated in the ordinary manner by means of magnesia mixture, sulphuretted hydrogen was passed into the ammoniacal filtrate until the liquid had assumed a bright red colour. All the molybdic acid was then precipitated as sulphide by the addition of hydrochloric acid, not a trace remaining in solution. The sulphide was then persistently washed with water containing sulphuretted hydrogen and hydrochloric acid, rinsed down from the filter into a broad platinum capsule; the residue adhering to the filter was oxidised by the vapour of bromine, dissolved in water, and added to the main portion. After careful stirring and repeated evaporation with a mixture of dilute sulphuric and nitric acids, driving off the acids by heat, and carefully igniting the residue to very dull redness, all the sulphide was oxidised to molybdenum trioxide. In order to expel any residues of suiphuric acid and to prepare the substance for weighing, it was transferred to a platinum crucible, the capsule was washed with dilute ammonia, and the solution poured into the crucible. By cautious evaporation, very gradual heating, and final ignition to dull redness, the molybdic acid was obtained pure. It appeared as a dense powder—bright yellow when hot, almost white when cold—and after cooling in the exsiccator it was weighed.

The direct determination of the ammonia by distilling the phosphomolybdate with soda-lye and titrating the distillate gave no satisfactory results. An indirect determination by saturating the salt with standard ammonia or soda was found to be practicable and convenient. By means of this method, which will be described in full in the sequel, the acids present in unstable combination were determined.

The proportion of phosphoric acid in the precipitate dried at 150°, of different preparations, and found on microscopic examination to contain no free molybdic acid, fluctuated between 3·72 and 3·77 per cent. The molybdenum trioxide was found 91·86 to 92·11. The formula $12MoO_3.PO_4.(NH_4)_3$ would require 3·78 P_2O_5 and 91·75 MoO_3 (O = 16, Mo = 96).

In accordance with these values the weight of an ammonium phosphomolybdate, ascertained by a method to be described below and dried at 150°, obtained by precipitating a known weight of phosphoric acid by 24 mols. or an excess of molybdic acid, amounted to 26·90 to 26·65 times the weight of the phosphoric acid employed, corresponding to a proportion of 3·72 to 3·75 per cent, which was in two cases confirmed by analysis, the weight obtained being 3·74 per cent P_2O_5.

The precipitates thrown down with an excess of acid, washed with diluted acid, and dried for several weeks in the exsiccator over calcium chloride and caustic potassa until the weight was constant, lost, when heated to 130° to 150° (giving off moist strongly acid vapours), in weight.

The nitric acid compound, 7·13 per cent = 7·67 per cent, on the substance dried at 150°.

The hydrochloric compound, 4·78 per cent = 5·02 per cent, on the substance dried at 150°.

For saturating the precipitate obtained with nitric acid were required for salts dried in the exsiccator 23·03 per cent, corresponding to 25 43 mols., or 53·89 NaOH corresponding to 25·28 mols. After heating to 150°, 20·96 per

cent NH_3, corresponding to 23·14 mols., or 50·01 per cent NaOH, corresponding to 23·46 mols. (All referred to 1P).

The salt precipitated by hydrochloric acid was neutralised, when dried in the exsiccator, by 54·01 per cent NaOH = 25·34 equivs.; after heating to 150° by 49·92 NaOH = 23·42 equivs.

These numbers, for the sake of direct comparison, have been re-calculated for the dry substance free from acid. Triammoniumphosphododekamolybdate would require for saturation 23 equivs. of alkali.

As we see, the precipitates dried in the exsiccator require for neutralisation about two equivalents more alkali than those dried at 150°, corresponding to as many equivalents of nitric or hydrochloric acid in combination with the phosphomolybdate. In point of weight 2 mols. NO_3H would amount to 6·71 per cent, and 2 mols. HCl to 3·89 per cent if referred to 100 parts of phosphomolybdate free from acid and water. If the numbers found as loss of weight on heating to 150°, the salts previously dried in the exsiccator, are diminished by these amounts, there remain for water 7·67 − 6·71 = 0·96 per cent and 5·02 − 3·89 = 1·13 per cent, of which figures the former represents exactly, and the latter approximately, a mol. of water. The precipitate dried in the exsiccator has consequently, according to the acid used in its precipitation and washing, the composition—

$$12MoO_3.PO_4.(NH_4)_3.2NO_3H.H_2O \text{ or}$$
$$12MoO_3.PO_4.(NH_4)_3.2ClH.H_2O.$$

The author has not made a determination of the proportion in the precipitate, as the compound, if washed, neutrally undergoes a change if it remains any length of time in a moist condition.

2. *Influence of the Proportion of Ammonium Salt (Nitrate) in the Solution upon the Separation of the Precipitate.*

For these experiments the following standard liquids were employed:—

Solution A.—5·043 grms. sodium hydrophosphate per litre, therefore 0·001 grm. P_2O_5 per c.c.

Solution B.—Neutral sodium molybdate, 0·010 grm. per c.c.

Solution C.—Ammonium nitrate, 0·010 NO_3NH_4 per c.c.

Solution D.—Nitric acid, 0·10 grm. NO_3H per c.c.

Of the solutions A and B known volumes were mixed, so that phosphoric and molybdic acid were present in some experiments in the molecular proportion 1 : 24, or in some cases in a different proportion. In some cases the solution was further concentrated by evaporation, and in others diluted by the addition of water. A measured quantity of the nitric acid D was then added, the yellow liquid was heated almost to a boil, and a solution of ammonium nitrate was very gradually run in, stirring all the time with the glass rod until the precipitate of ammonium phosphomolybdate no longer increased.

During the formation of the latter the following phenomena were observed:—At first the precipitate disappeared again regularly if the observer waited a short time after the addition of every drop of ammonium nitrate. It did not become permanent until a considerable part of the solution had been added, though it still increased visibly with every drop of the ammonium salt added, and soon gave the solution a pale yellow, milky appearance. In this state, which resembled an emulsion, the liquid did not clear in the slightest, even after prolonged heating, and on the attempt to filter it ran through very turbid.

But now a few more drops of the ammonium nitrate generally sufficed to condense the precipitate and to cause it in time to deposit, so that the solution, if viewed against a blue glass, appeared clear. Further addition of ammonium nitrate occasioned no precipitation; the separation of the phosphomolybdic acid was completed, and the solution quite colourless.

The quantity of ammonium nitrate consumed was noted, the final volume of the liquid determined, and it was calculated how much ammonium nitrate was present in 100 c.c. of the solution. It now appeared that this quantity, within the limits of the experiment, independently of the proportion of phosphoric, molybdic, and nitric acids, was always essentially the same, *i.e.*, about 0·4 to 0·5 grm. ammonium nitrate in 100 c.c. If the quantity was smaller than 0·4 grm. the liquid remained milky and could not be filtered. With more than 0·5 grm. in 100 c.c. the separation of the phosphomolybdic acid (unless the solution contains less than 0·01 grm. phosphoric acid per 100 c.c.) in a number of minutes, the more rapidly the more phosphomolybdic acid was present.

In order to effect the most rapid separation of the phosphomolybdate, it seemed most convenient to have from 5 to 10 per cent of ammonium nitrate.

In a similar manner the quantity of potassium nitrate necessary for the precipitation of the phosphododekamolybdic acid as a potassium salt was determined. It was found that the precipitation (apparently independent of the other conditions) is not complete until the liquid contains 1·76 grm. NO_3K in 100 c.c. To throw down the phosphomolybdic acid there are required—

$$\frac{1·76}{101} : \frac{0·45}{80},$$

or about three times as many mols. potash salt as mols. ammonium salt.

It was interesting to know the influence of the relative proportions of ammonium and potassium salt in the solution upon the composition of the precipitate.

3. *The Conditions of Temperature and Concentration.*

These conditions have been but little studied. In accordance with Stünkel, Wetzke, and Wagner, the author found that under otherwise favourable conditions the temperature had no influence upon the completeness of the separation of the phosphomolybdate. The precipitation was the more rapid the more of the elements of phosphomolybdic acid was present and the more strongly it was heated.

Thus, in solutions which contained not more than 0·05 grm. P_2O_5 in 100 c.c., the precipitate fell down almost instantly on heating to near the boiling-point and adding solution of molybdic acid, whilst in the cold a precipitate appeared, indeed, at once, but required for its complete separation from half an hour to an hour.

0·010 grm. P_2O_5 in 100 c.c. of liquid which were completely precipitated from a hot solution in a few minutes, formed at common temperatures the first traces of a precipitate in the shape of delicate stripes and veils on the sides of the glass after the solution had stood for ten minutes with frequent stirring. (How considerable may be the influence even of slight differences of temperature is shown by the observation that these cloudings appear most plainly at those parts of the side of the vessel at which the heat of the body has been communicated to the liquid by contact with the hand). The separation then became slowly more copious, and was almost complete in two and a half hours. But even after twelve hours traces of phosphomolybdic acid remained in solution, and their separation had to be assisted by heat and agitation.

Stirring and rubbing with the glass rod, promote, in all cases the separation. Under certain circumstances this mechanical impulse is necessary to set up the reaction.

As for the physical properties of the precipitates obtained at different temperatures and under other varying conditions, those thrown down from very hot and not too acid solutions and with an excess of molybdic acid seemed to the author, on microscopic examination, the most perfectly crystalline. The presence of a sulphate seems to favour the crystalline development of the precipitate, but delays its separation.

The precipitate from a cold solution is composed of

spheroidal granules of very different sizes. That from hot solutions is very uniform in its grain and consists of distinctly formed octohedrons.

This is the reason why the precipitate from a hot solution settles more quickly and more completely and can be more easily filtered and washed without loss than that thrown down in the cold, whose finest particles can remain for a long time in suspension, and can pass through the pores of the filter.

4. *Influence of the Degree of Acidity of the Solution upon the Formation of the Phosphododekamolybdate.*

If we allow dilute nitric acid gradually to flow into a neutral solution containing the elements of phosphododekamolybdic acid along with a suitable quantity of ammonium nitrate, applying heat, we observe the following phenomena :—

In the first place the liquid remains completely clear and colourless, but, on the further addition of acid, there appear yellow colourations and turbidities, which, on stirring, disappear in a short time. Then follows a permanent yellow colour, at first pale, but becoming more and more intense, with incipient precipitation, then copious yellow deposits which subside at first slowly, but more and more perfectly on further acidification. Finally, a visible precipitation is no longer produced, but there still ensue in the liquid, as it becomes clear, slight deposits. After a few more drops the separation of the yellow phospho-molybdate is complete.

A further slight addition has no influence on the precipitate, but a considerable excess produces a decomposition the more decided the greater the excess.

More manifest is this decomposing action of an excess of acid if it is allowed not to act upon the pre-formed phospho-molybdate, but is added to the phosphoric or the molybdic solution before they are mixed together.

Whilst in a solution of a proper degree of acidity P_2O_5 is thrown down quantitatively by 24 mols. MoO_3; in strongly acidified solutions double the quantity, and more of molybdic acid may be consumed before any precipitation appears. Not until the injurious excess of acid has been neutralised does the liquid deposit all its phosphomolybdic acid, which had previously existed in a dissociated condition. The dissociated phosphomolybdic acid can also be caused to separate by an excess of molybdic acid, which must be the larger the more acid the liquid.

(To be continued).

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

In a report presented to the Bath Meeting the Committee gave an account of the replies they had received to a letter addressed to the head masters of schools in which elementary chemistry is taught. In this letter the Committee had asked for a report on the chemical teaching, and also for a statement as to the methods which had been found to render the teaching most effective as a mental training. In commenting on these replies the Committee pointed out that the evidence which had been collected was conclusive in showing that much of the teaching of elementary chemistry is far from satisfactory, and needs to be considerably modified if it is to effect that valuable mental discipline which science teaching can afford.

The Committee are convinced that the high educational value of instruction in physical science has never been exhibited to its full advantage in most of our educational institutions. Nevertheless there exists already a considerable body of experience which proves that there is no more effective and attractive method of training the logical faculties than that which is afforded by a properly arranged course of instruction in physical science; by no other means are the powers of accurately ascertaining facts, and of drawing correct inferences from them, so surely developed as they are by the study of this subject.

Since the last meeting the Committee have been actively engaged in discussing the lines which a course of elementary instruction in chemistry should follow. The Committee were the more inclined to offer suggestions of their own, since they had learnt from the replies made to their letter of last year, by teachers in many of our well-known schools, that not only is the necessity for the adoption of improved methods fully recognised, but that teachers are anxious to receive advice and assistance in introducing them.

It cannot be too strongly insisted that elementary physical science should be taught from the first as a branch of mental education, and not mainly as useful knowledge. It is a subject which, when taught with this object in view, is capable of developing mental qualities that are not aroused, and indeed are frequently deadened, by the exclusive study of languages, history, and mathematics. In order that the study of physical science may effect this mental education, it is necessary that it should be employed to illustrate the scientific method of investigating nature, by means of observation, experiment, and reasoning with the aid of hypothesis; the learners should be put in the attitude of discoverers, and should themselves be made to perform many of the experiments. The lessons ought to have reference to subjects which can be readily understood by children, and illustrations should be selected from objects and operations that are familiar to them in everyday life. Chemistry is particularly well adapted for affording this kind of instruction, and the Committee are of opinion that a course which is mainly chemical will be most useful in developing logical habits of thought.

Chemical inquiry involves, however, the use of various physical processes, and these are themselves of great value from the point of view from which the instruction is being given. It is also of great importance that the learners should become acquainted with the characteristic instrument of physical science, viz., measurement, and therefore quantitative processes should be largely made use of.

Having agreed as to the general principles on which a scheme of elementary instruction in chemistry should depend, the Committee gladly accepted the offer of Professor Armstrong to draw up an account of such a scheme in sufficient detail to serve as a guide to those who have to provide such teaching. Without pledging themselves to accept all its details the Committee consider that the scheme which Professor Armstrong has prepared (see below) is in general accordance with their views as to what should constitute a course of elementary instruction in physical science.

With regard to the manner in which the scheme should be carried out, the Committee wish to lay stress on the following points. In order that the plan should produce its full educational effect, the instruction should be commenced at an early age, and be extended to every child in the school. They do not desire to bring forward physical science as a substitute for any of the other principal subjects of study, but they ask that, like these subjects, it should be looked upon everywhere as a necessary part of education, and that it should receive a due share of the time devoted to school work. It is well known that at present science-teaching does not generally receive as much time and attention as is given to other studies,

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

This was made clear in the report of the Committee last year. It will be necessary to allot more time to the subject, and to employ a greater number of teachers. A teacher should not be required to give practical instruction to more than from fifteen to twenty pupils at one time, although the classes at lectures and demonstrations might be somewhat larger.

While the scheme now proposed may involve the employment of a larger number of teachers of natural science, on the other hand fittings and apparatus of the simplest description are all that will be absolutely needed, and the cost of maintenance will be relatively small.

The Committee are aware that the course of instruction now suggested is not in conformity with the present requirements of examining bodies. Its general adoption must therefore depend on their co-operation.

Suggestions for a Course of Elementary Instruction in Physical Science. Drawn up by Professor ARMSTRONG.

Although the Committee is ostensibly charged to report as to methods of teaching *chemistry*, chemistry pure and simple is not what is required in schools generally, and therefore the Committee must be prepared to take into consideration and make recommendations as to a course of instruction preliminary to the natural science course proper, which in their opinion affords the most suitable and efficient preparation for later natural science studies.

After the most careful consideration of the question during at least ten years past, and after long holding the opinion that chemistry, as usually understood, is not the most suitable science subject for school purposes, I am now of opinion that a course which is mainly chemical is not only the best, but also the only one possible if we are to secure all the objects aimed at in introducing science teaching in schools. Those objects are essentially: to train boys and girls to use their brains; to train their intelligence; to make them observing and reasoning beings, accurate observers and accurate thinkers; to teach them to experiment, and that, too, always with an object—more frequently than not with what may be termed a logical object—not for mere descriptive purposes; to gradually inculcate the power of "doing," on which Charles Kingsley has laid so much stress, and which undoubtedly is the main factor of success in life. It can scarcely be gainsaid that through chemistry more than through any other branch of natural science it is possible to give precisely that kind of "practical" training so requisite at the present day, because the student is able to ascertain *by experiment* what are the exact facts, and thus to arrive independently at an explanation, whereas in the case of other sciences, more often than not the explanation of necessity has to be given by the teacher.

Chemistry as usually taught loses greatly in educational value because pupils are told, more often than not, that "so and so is the case," instead of being taught *how it has been found out* that such is the case; indeed, that which has to be proved is usually taken for granted. Practical chemistry has hitherto, as a rule, been interpreted to mean the preparation of a few gases, &c., and the analysis of simple salts. Much useful information may be and is occasionally imparted during the performance of exercises of this kind, but the tendency undoubtedly is for analysis to degenerate into a mechanical drill, and, looking at the question from the practical point of view, and, considering what is the general outcome of such teaching, probably we are bound to agree that the results thus far obtained are usually unsatisfactory. The difficulty, however, is to devise a course sufficiently simple both in conception and when carried into practice, the cost of which is not too great; but with respect to this item of cost the Committee has to make clear to parents and teachers the claim of natural science to a fair and proportionate share of the total expenditure, which certainly has never yet been granted to it. By the introduction of such studies into the school course a set of faculties are trained which it is all-important to develop, but which hitherto have been allowed to remain dormant, if not to atrophy, through neglect, and which, it is admitted by all competent authorities, cannot possibly be developed by any amount of attention paid to literary and mathematical studies. It is often not sufficiently clearly stated or understood that the advocates of natural science studies have no desire to displace any of the traditional subjects from the school course, and that all that they ask for is a fair share of the child's time, attention, and brains—a share proportionate to the effect which such studies can demonstrably produce in developing the mental faculties of the individual: that, in fact, natural science claims to co-operate and in no sense puts in an appearance as a rival.

STAGE I.—*Lessons on Common and Familiar Objects.*

The first stage of instruction must be one of simple object lessons, but these should have an intimate relation to the child's surroundings, and should be made the pegs on which to hang many a tale. Probably the most satisfactory and practical mode of commencing is to get children to draw up lists of familiar and common objects under various heads, such as—

Natural objects.

Things used in building construction.

Things from which household furniture is made or which are in daily use.

Things used as clothing.

Food materials.

The children should be induced to describe these from observation as far as possible; to classify them according to their origin into mineral and animal and vegetable or organic; and occasion should be taken at this stage to give, by means of reading lessons and demonstrations, as much information as possible about the different things, their origin, how made, and their uses. It is obvious that in this way a great deal of geography and natural history (*Naturkunde*) might be taught in an attractive manner. Geikie's "Science Primer on Physical Geography" is the type of book which may be worked through with great advantage at this stage.

STAGE II.—*Lessons in Measurement.*

This stage should be entered upon as soon as children have learnt the simple rules of arithmetic, and are able to add, subtract, multiply, and divide—and to use decimals.

Lineal measurements may be first made, using both an an English foot-rule with the inch subdivided in various ways, and a metric rule subdivided into millimetres. In this way the relation of the two scales is soon insensibly learnt.

Measurements of rectangular figures and the calculation of their areas may then be made.

After this the use of the balance may be taught, and the relation between the French and English systems may be learnt by weighing the same objects with the two kinds of weights. Use may then be made of the balance in determining the areas of irregular figures by cutting out rectangular and irregular figures from the same cardboard or thin sheet metal, and weighing these, &c.

Solid figures are next studied: a number of cubes made from the same wood having been measured, their volumes are then calculated, and the results thus obtained are compared with those which are obtained on weighing the cubes. The dimensions and weights of cubes made from different woods or other materials are then ascertained, and thus it is observed that different materials differ in *density*. The study of the *relative density* of things generally is then entered upon. The ordinary method is easily learnt and used by children, a suitable bottle being provided by filing a nick down the stopper of a common two-ounce narrow mouth bottle; it may then be shown that the same results are obtained by the hydrostatic method of weighing in air and water, and it is not diffi-

cult to lead children to understand this latter method after they have determined the heights of balancing columns of liquids, such as turpentine, water, and saturated brine, of which they have previously ascertained the relative density. These hydrostatic experiments are of value at a later stage in considering the effects of atmospheric pressure.

By determining the dimensions of a cube and the weight of the water which it will displace, an opportunity is afforded to point out that if the results are expressed in cubic centimetres and grammes respectively there is a practical agreement between the numbers, and hence, to explain the origin of the metric system of weights and the relationship between its measures and weights; the irrationality of the English system may then be explained.

The relative densities of a large number of common substances having been ascertained, the results may be tabulated and then the value of the data as criteria may be insisted on; as an illustration of their value, quartz, flint, sand, and gravel pebbles may be selected. The children having determined their relative densities, the agreement between the results may be pointed out and the identity of the material explained. By drawing perpendiculars corresponding in height to the densities of various substances, a graphic representation is obtained which serves to bring out the value of the graphic method of representation.

A very valuable exercise to introduce at this stage is based on the well-known fact that in certain conditions of the atmosphere things appear moist: a muslin bag full of seaweed may be hung up under cover but freely exposed, and may then be weighed daily at a given time; simultaneously the state of the weather, direction of the wind, the height of the barometer, and the wet and dry bulb thermometer may be noted; on tabulating the results, and especially if the graphic method be employed, the variations and their relationship will be noticeable.

The thermometer, having thus become a familiar instrument, may be used to examine melting ice and boiling water; the construction of both the Centigrade and Fahrenheit thermometer may then be explained, and the effect of heat on bodies made clear. The density of ice and of water at various temperatures may then be determined, a Sprengel tube—which is easily made—being used for warm water; the bursting of pipes in winter, the formation of ice on the surface of water, &c., may then be explained. Afterwards, simple determinations of the heat capacity of a few metals, &c., and of the latent heat of water and steam, may be made in accordance with the directions given in a book such as Worthington's "Practical Physics."

Stage III.—*Studies of the Effect of Heat on Things Generally; of their Behaviour when Burnt.*

As it is a matter of common observation that heat alters most things, the effects of heat on things generally should be studied; in the first instance qualitatively, but subsequently, and as early as possible, quantitatively. Bits of the common metals may be heated in the bowl of an ordinary clay pipe plunged into a clear space in any ordinary fire, or in such a pipe or a small iron spoon over a gas-flame. The difference in fusibility is at once apparent, and in the case of metals like iron and copper it is noticeable that although fusion does not take place, a superficial change is produced; the gradual formation of a skin on the surface of fused lead and tin is also easily perceived. Observations like this become of great importance at a later stage, and indeed serve to suggest further experiments: this is a point of special importance, and from the beginning of this stage great attention should be paid to inculcating habits of correct observation; the effect should first be recorded by the pupil, the notes should then be discussed and their incompleteness pointed out, and they should afterwards be re-written. The fusibility of substances which are not affected when heated in the tobacco-pipe may be tested by heating them with a Fletcher gas blowpipe on charcoal, and by heating little bits of wire or foil in such a flame it is easy for children to discover the changes which metals undergo when burnt, especially in cases such as that of zinc or copper or iron.

The further study of the effect of heat should be quantitative, and may well commence with water. It being observed that water disappears on heating, water may be put into a clock-glass or glass dish placed on a water-bath (small saucepan); it evaporates and it is then observed that something is left. A known quantity of water by weight or volume is therefore evaporated and the residue weighed. This leads to the discovery that water contains something in solution. The question then naturally arises, What about the water that escapes? so the steam is condensed and the distilled water evaporated. The conception of pure water is thus acquired. An experiment or two on dissolution—using salt and sugar—may then be introduced, a water oven or even an air oven (a small Fletcher oven) kept at a known temperature being used, and the residue dried until the weight is constant. Rain and sea water may next be examined; the results afford an opportunity of explaining the origin of rain and of accounting for the presence of such a large quantity of dissolved matter in sea water. Then the various common food materials may be systematically studied, commencing with milk; they should first be dried in the oven, then carbonised and the amount of char determined, then burnt and the percentage of ashes determined. A small platinum dish, 15 to 20 grms. in weight, is required for these experiments, and a gas muffle furnace is of the greatest use in burning the char and in oxidising metals. In addition to the discipline afforded by such experiments a large amount of valuable information is acquired, and the all-important fact is established that food materials generally are combustible substances. Afterwards mineral substances are examined in a similar manner, such as sand, clay, chalk, sulphur, &c., and then metals, such as lead, copper, tin, and iron may be studied; their increase in weight is in striking contrast to the inalterability of substances like sand and salt, and the destruction of vegetable and animal substances. Chalk, from which lime is made by burning, is found to occupy a middle position, losing somewhat in weight when strongly heated. The exceptional behaviour of coal among mineral substances, and of salt among food materials, is shown to be capable of explanation, inasmuch as coal is in reality a vegetable and salt a mineral substance; but sulphur remains an instance of exceptional behaviour requiring explanation. It is not exceptional in being combustible as metals like magnesium and zinc are combustible, but in affording no visible product. The smell of burning sulphur, however, serves to suggest that perhaps after all there is a something formed which is an invisible substance possessed of an odour, and then follows quite naturally the suggestion that perhaps in other cases where no visible or perceptible product is obtained—as on burning charcoal, for instance—there may nevertheless be a product. Whereas, therefore, in Stage I. the pupil will have learnt to appreciate the existence of a great variety of substances, and will have gained the power of describing their outward appearance more or less fully; and in Stage II. having learnt how to measure and weigh, will acquire the habit of determining by measurement certain properties of substances, and will thus be in a position to express in exact terms the kind of differences observed; in Stage III. the pupil will be led to see that profound changes take place on burning substances, and that these changes involve something more than the destruction of the things burnt. The foundation is thus laid for the study of change, *i.e.*, chemical studies proper.

Stage IV.—*The Problem Stage.*

Many of the changes observed in the course of the experiments made in Stage III. might be examined and

their nature determined, but the best to take first is a very familiar case, that of the rusting of iron.

Problem I. *To Determine what Happens when Iron Rusts.*—The pupil *must* be led in the first instance to realise that a problem is to be solved and that the detective's method must be adopted and a *clue* sought for. It is a familiar observation that iron rusts, especially when wet; what happens to the iron, why does it rust, is the iron alone concerned in the change? No information can be gained by looking at it—perhaps the balance which has brought to light so much in Stage III. may be of service, so the iron is allowed to rust in such a manner that any change in weight can be observed. A few grms. of iron-filing or borings are put on to a weighed saucer or clock-glass along with a bit of stiff brass or copper wire to be used as a stirrer; the iron is weighed, then moistened and exposed under a paper cover to keep off dust, preferably in a warm place; it is kept moist and occasionally stirred. After a few days it is dried in the oven and then weighed. The weight is greater. *Something from somewhere has been added to the iron.* Thus the clue is gained. Where did this something come from? The fact that when a tumbler, for instance, is plunged mouth downwards into water the water does not enter, and that on gradually tilting the tumbler to one side something escapes—viz., air—at once affords a demonstration of the presence of air in the space around us. The iron rusted in this air, but was kept moist, so it may have taken up the something from either the air or the water. To ascertain whether the air takes part in the rusting, some iron borings are tied up in a bit of muslin and the bag is hung from a wire stand placed in a (jam) pot full of water and a so-called empty (pickle) bottle, which in reality is full of air, is inverted over the iron; in the course of a few hours, as the iron rusts, the water is observed to rise until it occupies about one-fifth of the jar (determined by measuring or weighing the water); the something added to the iron during rusting appears therefore to come from the air, and the all-important fact is thus discovered that the rusting is a change in which not the iron alone, but also the air, is concerned. The experiment is several times repeated, fresh iron being used with the same air and the same iron put in succession into fresh portions of air, but the same result is always obtained: whence it follows that whatever it is in the air which takes part in the rusting, the air as a whole is not active. The changes previously observed to take place when iron, copper, lead, zinc, &c., were heated in air, are then recalled; as the metals were found to increase in weight it would appear probable that in these cases of change also the air was concerned.

These results at once suggest the question, What is air? So much having been learnt by studying the change which iron undergoes in rusting, other changes which happen in air therefore are next studied.

Problem II.—*To Determine the Nature of the Changes which take place on Burning Substances in Air.*—The use of phosphorus is introduced by reference to a match. Phosphorus is then burnt under a bell jar over water and the result noted: the disappearance of some of the air again shows that the air is concerned. The fact that phosphorus smokes when taken out of the water in which it is always kept suggests that some change is going on, so a stick of phosphorus is exposed in air as in the previous experiment with iron; soon one-fifth has disappeared and the phosphorus then ceases to smoke. The *quantitative* similarity of the two results suggests that iron and phosphorus behave alike towards air and *vice versâ*, and serves to confirm the idea that some constituent of the air present only to the extent of about one-fifth is active. But nothing is to be taken for granted, so iron is exposed in the phosphorus-air residue and phosphorus in the iron-air residue: as no change occurs there is no room left for doubt. Recalling the experiments in which various metals were burnt in air in order to determine whether in these cases the same constituent of the air was concerned in the change, air from which the active constituent has been removed by means of phosphorus, is passed through a heated tube containing bits of the metals: no change is observed, so it is evident that as a rule, if not always, one and the same constituent of air is concerned. The experiments with iron and phosphorus, although they show that the air is concerned in the changes which are observed to take place, do not afford any information whether or no the water which is also present is concerned in the change. Phosphorus is therefore burnt in a "Florence" flask closed with a rubber stopper: on removing the stopper under water some water enters, and by measuring this and the amount of water which will fill the flask the same result is obtained as in the previous cases. To be certain whether in this case anything enters or escapes from the flask it is weighed before and after the phosphorus is burnt. There is no change in weight. But does nothing escape? Yes, much heat; whence it follows that heat is not material: that, although some of the air disappears, it is merely because it has become affixed to or absorbed by something else. This has been proved in the case of the rusting iron and the burnt metals. To obtain indisputable evidence in the case of the phosphorus this is burnt in a current of air in a tube loosely filled with asbestos to retain the smoke: the weight is round to increase. The observation that the phosphorus ceases to burn after a time suggests the introduction of a burning taper into the residue left by iron, &c.; it is found to be extinguished. Then a candle and subsequently a gas flame may be burnt in a bell jar full of air over water. Reversed combustion may then be demonstrated in order to fully illustrate the reciprocal character of the phenomena. Thus it is ascertained that in all ordinary cases of combustion are changes in which the air, and not the air as a whole, but a particular constituent, is concerned, and no doubt remains that the same constituent is always active, but active under different conditions; it is realised also that the production of heat is the consequence of the union of the substance burnt with the active substance in air. The experiment of exposing phosphorus in air affords the opportunity of demonstrating the evolution of heat even in a case where no visible combustion occurs, as the phosphorus is always observed to melt. At this stage careful note should be taken of the appearance of the different products of combustion and of a change such as that which occurs when the product from phosphorus is exposed to the air.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Nots.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 9, August 26, 1889.

The Relations of Atmospheric Nitrogen to Vegetable Mould. A Reply to M. Berthelot.—Th. Schlœsing.—M. Berthelot, in invoking the results of MM. Dehérain, Hellriegel, Wilfarth, Breal, and Frank in support of his conclusions, confounds two distinct questions—the fixation of gaseous nitrogen by vegetable mould, and the fixation of gaseous nitrogen by certain vegetable species. The author has merely dealt with the former question, whilst the observations and experiments of the authorities cited concern specially the latter question, and do not solve the former. He maintains his former conclusions, *i.e.*, that he has not succeeded in witnessing the fixation of nitrogen by bare vegetable mould without vegetation, though experimenting under the very same conditions which M. Berthelot has observed.

Action of Water upon Stannic Chloride.—Leo Vignon.— If stannic chloride is mixed with water the result is a solution of stannic oxide in dilute hydrochloric acid. This stannic oxide, which is very unstable, tends to become polymerised. In time the polymerisation reaches a certain state of equilibrium, which is a function of the dilution, the temperature, and the chemical composition of the liquid.

The Action of Phosphates upon the Cultivation of Cereals.—G. Raulin.—It is probable that in agricultural practice we may employ the natural tribasic phosphates containing phosphoric acid in the so-called insoluble state if the former are applied in large proportions varied according to the crops and the nature of the soil for the first years.

No. 10, September 2, 1889.

Researches on the Relations Existing between the Colour of Plants and the Richness of the Soil in Agents of Fertility.—Georges Ville.—The author has studied the colour of the leaves of plants in the time before flowering, in connection with the fertility of the soil. He finds that this colour experiences a decided change if one of the four constituents of his "complete" manure is wanting in the soil. Its intensity increases or decreases; the colour remains green or turns yellow according as the soil is wanting in phosphate, in potassa, or in nitrogen. He has fixed the exact shade by the aid of Chevreul's chromatic circles. In plants which especially require nitrogen the leaves turn yellowish in its absence. For greater precision he compares the colouring-matter extracted and diluted in a constant volume of alcohol. He first removes the erythrophyll (carotine) by treatment with petroleum ether, and then extracts the leaves with absolute alcohol, which takes up all the chlorophyll. The liquids thus obtained are then compared.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xix., No. 12.

The Origin of Bronze and the Sceptre of Pepi I., King of Egypt.—M. Berthelot.—Already noticed.

The Use of Cold in the Preparation of Pharmaceutical Extracts.—L. A. Adrian.—From the *Bulletin Soc. Chim. de Paris.*

MISCELLANEOUS.

Manures and Their Uses.—Dr. A. B. Griffiths's work on this subject has just been published by Messrs. George Bell and Sons.

Guy's Hospital.—The Open Scholarships in Arts have this year been awarded to Mr. William S. Handley, Loughborough Grammar School, and Mr. John Robert Steinhaeuser, Sutton Valence School. The Open Scholarships in Science have been awarded to Mr. John A. Howard, King's College and Guy's Hospital, and to Mr. Arthur H. Leete, University College, Aberystwith.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Manures.—Can any reader refer me to papers treating on chemical manure, shoddy manure especially?—H. Thompson.

Crystalline Metal.—Can any reader tell me if there is any known metal which crystallises from, and is precipitated from, solution as threads three or four inches long, of a golden and rose-red colour with metallic lustre?—Unknown.

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THE CHEMICAL NEWS.

Vol. LX. No. 1559.

ON THE

DETECTION OF ADULTERATION IN ESSENTIAL OILS.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

Our knowledge of the chemical properties of the majority of the essential oils is comparatively limited, notwithstanding the fact that many chemists have devoted a good deal of time to the investigation of these important substances. The most exhaustive research in connection with this subject of which I can find any record is that by Dr. Gladstone, the results of which are given in three papers published in the *Journal of the Chemical Society* (vol. xvii., p. 1; vol. xxv., p. 1; and vol. xlix., p. 609). In these papers Dr. Gladstone treats more particularly of the optical characters of nearly 60 kinds of essential oils, which he took great precaution to obtain in a perfectly pure condition. He gives the specific gravity, refractive indices, and rotation of the original oils; and, besides these data, he records the boiling-points, dispersion, sensitiveness, and specific refractive energy of certain hydrocarbons prepared therefrom. All three papers are full of useful information, and will well repay careful perusal.

Other valuable papers, dealing with various essential oils, have been published by Alder-Wright, Pattison-Muir, Tilden, Armstrong, Atkinson and Yoshida, Hartley and Huntington, Kingzett, and other chemists.

As most of the methods hitherto described in connection with the examination of essential oils have, as their main object, the qualitative detection of certain impurities and adulterants, *e.g.*, water and alcohol, I have recently investigated the subject from what is, I believe, a novel point of view so far as essential oils are concerned, in order to ascertain whether it is possible by any means not only to detect, but also to estimate, the proportion of such foreign ingredients.

For this purpose I purchased some 60 specimens, representing 26 of the most important essential oils occurring in commerce. It will, of course, be understood that it was necessary these oils should be of undoubted purity, or they would be useless for the object I had in view. I therefore communicated with some of the largest dealers in essential oils, and, having stated the nature of my proposed research, they undertook to supply me with the oils which I required. I may mention that the firms in question were the actual distillers of the majority of the oils, so the purity of most of these can, I think, be relied upon.

Two specimens, at least, of each kind of oil were examined, and in some cases several. In each of these oils I determined the specific gravity at 60° F., potash absorption, iodine absorption, and boiling-point.

With regard to the specific gravity determinations, although the figures from most of my duplicate samples agree fairly well among themselves, they do not, on the whole, correspond very closely with those obtained by Dr. Gladstone in his examination of similar oils.

The percentage of potash absorbed by each oil was ascertained by boiling a weighed quantity of the sample with an excess of seminormal alcoholic potash and titrating back with seminormal acid. Important results were obtained by this method of examination in the case of several of the oils.

The proportion of iodine absorbed by fixed fats and oils has been found so useful a factor in the detection of adulteration in those substances that I determined to estimate the iodine absorption of the essential oils which I was examining. To the best of my knowledge this test has never before been applied to essential oils—at any rate not to a large number of representative samples. The figures which I obtained by this method are in many instances highly instructive, and the boiling-point determinations will also be found to present some interesting features.

In the following table are recorded the results obtained by examining the oils in the manner indicated above:—

It will be seen from the above table that in many cases the two or more specimens of certain of the essential oils which I examined, although obtained from widely different sources, gave very concordant results. This remark applies more especially to the oils of bergamot, caraway, cassia, cedar-wood, cinnamon, citron, citronelle, cloves, lemon, mace, nutmeg, orange, thyme, and verbena.

On the other hand, the figures yielded by several of the oils compare unsatisfactorily with one another. This may possibly be due to actual adulteration of the oils in question, or to the presence of accidental impurities therein, or it may be caused by change in the composition of the oils through oxidation. The tendency of essential oils to become oxidised is well known, and it is probably due to this fact that what may be termed "the acidity expressed in terms of potash" appears so much greater in some of the oils than in others of the same kind—this liability to oxidation being, of course, more characteristic of some essential oils than of others, and depending to a considerable extent upon the mode and duration of storage. I ought, perhaps, to mention that one of my chief objects in undertaking this investigation was to see whether it was possible to discriminate by chemical analysis between the English and foreign varieties of those two highly important oils lavender and peppermint; because, if so, the results would be valuable from a commercial as well as from a scientific point of view. Unfortunately my hopes have not been realised so far as these particular oils are concerned. As a matter of fact, judging from the results which I have obtained, it would seem impossible to distinguish by the methods employed in this investigation between English and foreign oils of lavender, although an experienced person can easily detect an appreciable difference by the sense of smell.

The most striking difference between the two kinds of oil of lavender seems to be that French absorbs a larger quantity of potash than English, but without further investigation this can hardly be regarded as a characteristic feature. Addition of a considerable amount of "spike" oil to the more expensive oils of lavender would probably be indicated by a decrease in the boiling-point and in the percentage of potash absorbed by the mixture.

With regard to oil of peppermint, very little difference exists between the specific gravity, potash absorption, and boiling-point of the three varieties which I examined. There is, however, rather a wide divergence between the iodine absorptions, even between those of the same variety of peppermint oil. I am unable to offer any satisfactory explanation of these discrepancies, but there is no doubt about the accuracy of the figures, duplicate determinations being made in the case of all the oils.

The results obtained from the oils of lemon, citron, and orange are remarkably concordant and very interesting, both as regards pointing to the similarity of their respective constitutions and also as showing that adulteration of these valuable oils could be detected by chemical analysis.

It will be observed that oil of bergamot is the most acid of all the oils examined. This acidity I have found to be partly due to the presence of citric acid.

In speaking of the oils of cinnamon and cassia, Allen says ("Commercial Organic Analysis," vol. iii., p. 45):—"No sharp distinction exists between the two oils, or one which would enable one to be detected with certainty in presence of the other." This statement is contrary to my experience. There are, indeed, several striking points of

Name of Oil.	Specific gravity at 60° F.	Potash absorbed. Per cent.	Iodine absorbed. Per cent.	Boiling-point in ° F.
Aniseed—				
No. 1	0·976	0·25	274·44	434
No. 2	0·984	0·38	185·92	442
Bergamot—				
No. 1	0·879	11·43	247·90	374
No. 2	0·878	8·78	283·71	370
Cajeput—				
No. 1	0·918	0·35	70·85	490
No. 2	0·889	0·41	151·00	486
Caraway—				
No. 1	0·910	0·53	258·26	379
No. 2	0·913	0·35	263·22	388
Cassia—				
No. 1	1·061	10·17	75·06	490
No. 2	1·051	9·62	71·71	486
Cedar-wood—				
No. 1	0·952	0·92	78·51	518
No. 2	0·963	0·92	74·77	520
Cinnamon—				
No. 1	1·031	5·13	128·14	464
No. 2	1·021	4·91	105·05	466
Citron—				
No. 1	0·855	0·67	359·66	348
No. 2	0·871	1·90	320·04	346
No. 3	0·855	1·31	353 94	348
Citronelle—				
No. 1	0·893	3·35	186·30	416
No. 2	0·897	3·43	191·26	426
Cloves—				
No. 1	1·046	2·48	179·83	476
No. 2	1·041	2·35	155·46	478
Eucalyptus—				
No. 1	0·910	0·52	61·68	348
No. 2	0·910	0·36	106·46	350
No. 3	0·888	0·35	110·65	350
Juniper—				
No. 1	0·872	1·12	273·55	340
No. 2	0·878	0·84	236·09	344
No. 3	0·881	0·70	250·06	360
Lavender, English—				
No. 1	0·883	3·70	230·38	378
No. 2	0 887	3·17	248·59	374
No. 3	0·878	0·52	232·92	378
(Samples Nos. 1 and 2 are from Mitcham, Surrey, and No. 3 from Hitchin, Hertfordshire).				
Lavender, French—				
No. 1	0·893	4·85	198·65	378
No. 2	0·881	9·20	237·21	376
No. 3	—	4 90	199·18	—
Lavender, "Spike"—				
No. 1	0·873	1·99	287·90	330
No. 2	0·904	0·74	207·01	340
Lemon—				
No. 1	0·856	1·49	322·96	349
No. 2	0·858	1·41	320·16	352
Lemon grass—				
No. 1	0·897	2 25	223·24	432
No. 2	0·898	2·01	271·52	432
Mace—				
No. 1	0·886	0·85	220·85	346
No. 2	0·900	0·67	224·02	346
Nutmeg—				
No. 1	0·883	0·35	201·93	340
No. 2	0·898	0·19	206 24	342
Orange—				
No. 1	0·849	0·39	347·67	348
No. 2	0·853	0·38	341·75	351
Pennyroyal—				
No. 1	0·925	1·46	85·94	420
No. 2	0 939	4·62	78·58	418
Peppermint, Mitcham—				
No. 1	0·903	1·83	36·85	404
No. 2	0·908	1·97	46·37	407
Peppermint, American—				
No. 1	0·911	4·37	71·70	402
No. 2	0·904	2·71	53·09	400
Peppermint, Japanese—				
No. 1	0·900	2·29	56·06	400
No. 2	0·896	2·22	37·08	398
Rosemary—				
No. 1	0·894	0·78	161·67	335
No. 2	0·912	0·88	142·36	333
Rue—				
No. 1	0·860	0·56	192·02	338
No. 2	0·871	0·29	121·32	384
Sage—				
No. 1	0·961	7·09	49·70	360
No. 2	0·918	1·58	117·14	364
Sassafras—				
No. 1	1·056	0·33	162·68	430
No. 2	1·079	0·28	151·01	448
Thyme (red)—				
No. 1	0·892	1·91	181·48	338
No. 2	0·893	1·09	168·40	356
Verbena—				
No. 1	0·896	1·20	267·83	430
No. 2	0·895	1·37	247·81	430

distinction between the two oils, and, judging from the results of my experiments, it is evident that here, again, chemical analysis would be useful not only in detecting, but also in approximately estimating the proportion of adulteration in the case of the admixture of oil of cassia or other inferior oils with the more expensive oil of cinnamon. When it is remembered that the value of good oil of cinnamon is at least a dozen times that of oil of cassia the importance of this fact can hardly be over-estimated.

The greatest discrepancies of all occur between the two specimens of sage oil, and it is evident that there must be a considerable difference between their respective constitutions. According to Pattison-Muir (*Journal of the Chemical Society*, vol. xxxvii., p. 680) the composition of sage oil varies with the age of the sample. Soon after distillation comparatively small quantities of salviol, camphor, and cedrene are present, but as the oil increases in age the proportion of the two former bodies becomes larger and the $C_{10}H_{16}$ hydrocarbons decrease, while a hydrocarbon or hydrocarbons of the formula $C_{15}H_{24}$ is produced. This may, perhaps, account for the peculiar results which I obtained from the two specimens of sage oil which I examined.

When the costly nature of many of the essential oils is taken into consideration it is only to be expected that a good deal of adulteration will take place in connection with these substances. I understand that one of the cheapest, if not the cheapest, of the essential oils—citronelle—is largely sophisticated with kerosine oil, and the adulteration is said to be on the increase. What, then, must be the case with some of the more expensive oils, the price of which is enormous when compared with that of citronelle? There can be no doubt that the difficulty, and indeed, frequently, the impossibility, which has hitherto existed of detecting the presence of adulterants in essential oils by means of chemical analysis has led to an increase in this form of fraud. It is, therefore, gratifying to know that, by the use of the methods of examination which I have indicated above, the purity or otherwise of many essential oils can be determined with certainty.

Before concluding I should like to express my thanks to my assistants, Messrs. H. Winstanley and C. Boothby, for their valuable aid in the course of this investigation.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
September 14, 1889.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 170).

The Formation of Triammoniumphosphododekamolybdate from its Elements present in Neutral Solutions under the Influence of Nitric Acid.

THE author used in each experiment 0·010 grm. P_2O_5 and 0·243 grm. MoO_3, both bodies being consequently in the molecular proportion—

$$P_2O_5 : 24MoO_3.$$

The concentration of the nitric acid was taken, so that 0·04437 grm. NO_3H were present in the c.c., which quantity represented 10 mols. in reference to the P_2O_5 present, or 5 mols. if referred to the mol. of the phosphomolybdate to be precipitated The number of the c.c. nitric acid consumed multiplied by 5 showed how many mols. nitric acid were introduced every moment to one mol. ammoniumphosphomolybdate.

The mixture of the measured solutions of molybdate and phosphate was coloured with a little alkaline phenolphthalein, and was then accurately neutralised with dilute nitric acid. After adding a few grms. of neutral ammonium nitrate the whole was made up to 50 c.c. and, whilst constantly stirring, the standard nitric acid was added by drops from a burette and, with occasional interruptions (the solution being heated more and more, and ultimately, when there was no longer any fear of a loss of ammonia, nearly to a boil), until a distinct and permanent yellow colour appeared.

Here there were consumed 2·95—3·05 c.c. acid, or a mean of 3·00 c.c. = 15 mols.

Up to 3·30 the colour became constantly brighter, but the local precipitates disappeared again, all save a permanent unimportant turdidity.

From 3·35—3·45 c.c. (= 17 mols.) every drop occasioned a strong permanent precipitate up to about 4·50 to 4·60 c.c. = 23 mols. NO_3H, when the liquid began to grow clear.

Up to 5·10—5·20 c.c. only slight pale yellow precipitations were perceptible; beyond this limit (about 26 mols.) the precipitation of the ammonium phosphomolybdate was completed.

The following considerations will assist us in the interpretation of the three main phases of this reaction :—

The colourless liquid which represents the end of the first phase has exactly the properties of the solution we obtain on treating ammonium phosphomolybdate with ammonia, repeatedly evaporating off the liquid, renewing the water until no more ammonia is given off, and redissolving the colourless residue in water. This residue, which Hehner, *Zeitschrift*, xx., p. 292, recommends as a fit form for weighing, contains, according to him, when dry $_{24}P_2O_5$ = 3·509 per cent P_2O_5.

It is doubtless a mixture of hexammonium diphosphopentamolybdate and hexammonium heptamolybdate.

Fifteen mols. were found experimentally as the quantity of acid which is required to produce an incipient yellowness.

The second phase, between 15 and 17, is characterised by an increasing yellowness without permanent separation, and may be explained by the assumption of the formation of a soluble yellow intermediate product of the colourless soluble and of the yellow insoluble phosphomolybdate.

In the third phase, in presence of 6 more mols. NO_3H, the 7 mols. MoO_3 contained in heptamolybdate unite with the pentamolybdate to form phosphododekamolybdate.

The ultimate extension of the reaction to 23—26 mols. must be due to the two equivalents of nitric acid, which, as we are justified in assuming, form with the phosphomolybdate an unstable chemical combination, and to the small excess of nitric acid which promotes the completion of the separation.

It is to be noted that an excess of either component of phosphododekamolybdic acid in its original neutral solution involves an increased consumption of nitric acid, so that for every 6 mols. of $MoO_4(NH_4)_2$ present in excess there are required 11 mols. NO_3H, and for each mol. $PO_4H(NH_4)_2$ about 2 mols. NO_3H, for the separation of the phosphomolybdate more than if the substances had been mixed in the exact proportion—

$$P_2O_5 : 24MoO_3.$$

As for the first case 11 mols. of NO_3H are exactly the quantity which would convert 6 mols. $MoO_4(NH_4)_2$ into an acid molybdate containing $1NH_4$ to MoO_3. In the second case, 2 mols. NO_3H would be more than sufficient to convert the excessive hydrophosphate into dihydrophosphate.

These facts compel us to assume that the formation of the phosphododekamolybdate depends on the presence of monammonium hexamolybdate on the one hand, and dihydrophosphate on the other, and on a condensation of two mols. of the former body with one mol. of the latter, two mols. of water being eliminated. The yellow phosphododekamolybdic acid should therefore be a phosphodihexamolybdic acid.

Influence of an Excess of Nitric Acid upon the Formation and Dissociation of Phosphododekamolybdic Acid, and the Quantity of Molybdic Acid Requisite for its Separation.

1. The phenomena of the dissociation of phosphomolybdic acid have been studied in the following manner :—

Mixtures of 0·010 grm. P_2O_5 and 0·243 grm. MoO_3 were again employed. To prevent an undesirable increase of the volume the nitric acid was taken at ten times the strength, as in the former experiments, so that with each c.c. of acid 50 mols. of nitric acid were introduced to the mol. of the phosphomolybdate present in its elements. From obvious reasons the nitric acid could not be added to the complete mixture of phosphate and molybdate. There was first prepared a mixture of neutral molybdate with ammonium nitrate, the required quantity of nitric acid was added, the measured dose of phosphate solution run in with agitation, and in order to preserve in all cases the same molecular concentration for P_2O_5 and MoO_3 the liquid was made up to 60 c.c. To prevent any disturbing loss of acid by evaporation a condenser was connected with the flask during heating.

The solutions with slight excess of acid deposited the yellow precipitate in a few moments or minutes; in those richer in acid the precipitation was slower and less perfect, and where the excess of acid was very great it did not occur at all.

As soon, in each case, as the deposition had reached its maximum, indicated by the phenomenon that after removing the yellow matter from one part of the side of the glass subsequent rubbing with the stirring rod and prolonged heating did not lead to its re-formation, the hot liquid was filtered, the precipitate was washed with dilute nitric acid, containing ammonium nitrate, and the filtrate with the washings was saturated with ammonia down to the most desirable point of acidity.

The occurrence of a faint yellow colour without the subsequent settlement of a precipitate indicates traces of phosphoric acid and molybdic acid, which are contained in the filtrate in consequence of incipient dissociation. The dissociation, increasing with the acidity of the solution is indicated by the increase of the precipitates produced in the filtrate on neutralising the acid. They were brought upon the filter, and weighed in a manner which will be indicated below.

From the point when the separation of the phosphomolybdate from the neutral mixture by means of nitric acid is complete, *i.e.*, 26 mols. up to about 80 mols. (excess = 54 mols.) a dissociation could not be shown. The filtrate from a precipitate thrown down from a solution with 90 mols. became faintly yellow on neutralising the excess of acid. With 100 mols. (excess = 74) the dissociation was more perceptible; the filtrate, after partial neutralisation and concentration, gave traces of a precipitate. From this point the dissociation increased continuously and rapidly, and 2000 mols. nitric acid prevented the precipitation completely; the liquid was colourless, but turned yellow on the addition of a little ammonia, depositing at the same time a little phosphomolybdate. The limit of total dissociation was, therefore, not far overstepped, and would probably fall at about 1900 mols.

In a parallel experiment to determine what quantities of molybdic acid were needed at different degrees of acidity for the complete precipitation of the phosphoric acid, it appeared that the excesses going beyond the normal standard of 24 mols. MoO_3 (to 1 mol. P_2O_5) were almost exactly equal to the quantities of molybdic acid which, in the previous experiment, remained in solution in consequence of dissociation.

The measured volumes of the phosphate solution, acidified with varying quantities of nitric acid, and with the precautions laid down in Section 7, were mixed with a solution containing, per c.c., 0·010 grm. of free molybdic acid until the last drops no longer occasioned precipitation. The precipitates were heated with a further small excess of molybdic acid, washed, and weighed.

(To be continued).

THE MANUFACTURE OF PRUSSIATE OF POTASH.*

By J. B. READMAN, D.Sc., F.R.S.E.

The first portion of this paper refers to the present condition of this manufacture, describing the present process as very wasteful and imperfect, and shows that very little attention has of late years been devoted to improving the process, which has remained stationary for nearly half a century.

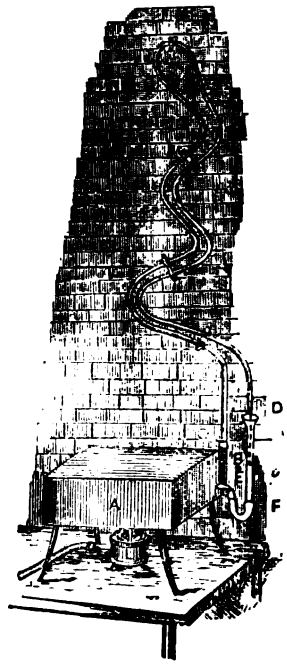
A general sketch of the process now employed in manufacturing prussiate is next given. Then follows a brief notice of the history of prussiate since its discovery last century, and of the processes that have been proposed or patented to improve the manufacture, and lastly, full details of a series of experiments made by the author to produce prussiate by the action of ammonia gas upon red-hot wood charcoal which had been previously saturated with carbonate of potash.

A CONSTANT WATER-BATH.

By Dr. BENNETT F. DAVENPORT.

A description of this apparatus will be found in the *Pharmaceutische Rundschau* for March, 1887, and in the *Proceedings of the American Pharmaceutical Association* for 1887. It has proven so satisfactory that I think it worth while to repeat the description here for the information of chemists. I have kept my bath boiling day and night seven days in the week, and have added water to it but five times in as many years.

It consists of the square box, A, supported over a Fletcher's solid-flame burner. The top of the box, 15 × 15·5 inches, is formed by a brass plate, ⅛ inch thick, which thus is stiff enough to support a considerable weight without yielding, the sides and bottom being sheet-copper. From the point B projects a ½ inch brass tube, B C, which turns up at a right angle. At E is a stop-cock, which is connected by a thick rubber tube with the glass tube, D F, which is fastened against the adjoining wall. Connected with C by a rubber joint is a ½-inch block-tin tube of 20 feet length, which extends up the wall in the manner shown to the highest point, T, and thence returns and ends just over the slightly funnel-shaped top of the glass tube at D. The bath being filled with water to just the level B *b*, may be kept constant by boiling for many days without appreciable loss of water,



the steam being condensed in its passage up, or if uncondensed before it reaches the point T, in its passage down the block-tin tube. In flat-bottomed platinum or porcelain capsules evaporation goes on very rapidly when placed on top of this water-bath. The whole surface of the bath is nickel plated.—*The Journal of Analytical Chemistry*, Vol. iii., Part 3.

CLASSIFICATION OF THE ATOMIC WEIGHTS IN TWO ASCENDING SERIES, CORRESPONDING TO THE GROUPS OF ARTIADS AND PERISSADS.*

By W. R. LIVERMORE, Major of Engineers, U.S. Army.

(Concluded from p. 166).

Table III. shows the deviations, arranged in the groups and series of the periodic law; the lower division shows the electro-chemical numbers in the same form.

Neglecting insignificant deviations, we find the positive results, or those where the atomic weight is slightly in excess of the serial number, either near the extremes of the electric series, in elements of maximum atomic volume, &c., or in the very centre of this series. The negative results occur half-way between the centre and the extremes. Of the perissads, 1, 2,—31, 32,—57, 59, are positive, and 17, 18, 19, 21,—44, 47, 54, 55, are negative; of the artiads, 7,—46, 51, 53, are positive, and 8, 14, 21, 23, 28, are negative.

* Read before the British Association, Section B, Newcastle Meeting.

* A Paper presented to the American Academy of Arts and Sciences, April 10, 1889.

In the periodic arrangement the first and second groups show positive deviations in the high series of this arrangement; the third, fourth, and fifth, negative in the high series; the sixth, positive in the high series; and the seventh, positive in two terms, and insignificant in two. The seventh and eighth groups are negative in the third series. The deviation of *Zn* is not included in these calculations, nor is the cause of its deviation yet apparent. Perhaps the perissads of the second group are formed from an artiad nucleus, and the artiads of the second group from a perissad nucleus, thus: * 65, 70, 75, 80, &c., and 63 * 71, 75, 79, &c. The last line shows the algebraic mean of the deviations in each group, which, as might be expected, corresponds nearly to the relative atomic volumes.

To do justice to the bearing of these results on the physical question of the ultimate nature of "atoms" would involve a mathematical discussion too prolonged for this paper; but the subject cannot be completed without a brief statement of its relation to well-known systems and theories of chemistry. A few extracts will serve as a basis to show what the perissad law is intended to contribute to the solution of the all-important problem.

In 1854, in a paper read before the American Academy on "The Numerical Relation between the Atomic Weights," Professor Cooke announced the character of the problem as follows:—

"Numerical relations between the atomic weights of the chemical elements have been very frequently noticed by chemists. One of the fullest expositions of these relations was that given by M. Dumas, of Paris, before the British Association for the Advancement of Science, at the meeting of 1851. This distinguished chemist at that time pointed out the fact that many of the elements might be grouped in triads, in which the atomic weight of one was the arithmetical mean of those of the other two. Thus the atomic weight of bromine is the mean between those of chlorine and iodine; that of selenium is the mean between those of sulphur and tellurium; and that of sodium, the mean between those of lithium and potassium.

"M. Dumas also spoke of the remarkable analogies between the properties of the members of these triads, comparing them with similar analogies observed in organic chemistry, and drew, as is well known, from these facts arguments to support the hypothesis of the compound nature of many of the now received elements. Similar views to those of Dumas have been advanced by other chemists.

"The doctrine of triads is, however, as I hope to be able to show in the present memoir, a partial view of this subject, since these triads are only parts of series similar in all respects to the series of homologues of organic chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number. All the elements may be classified into six series, in each of which this number is different, and may be said to characterise its series. In the first it is 9, in the second 8, in the third 6, in the fourth 5, in the fifth 4, and in the last 3." (See Table IV).

The paper speaks of the properties of the elements which are functions of the atomic weights, and says that it does not seem bold theorising to suppose that the atoms of the members of the same series are formed of a common nucleus, to which has been added one or more groups of atoms, or perhaps one or more single atoms, to which the corresponding element has not been discovered.

Referring to this subject in 1857,* M. Dumas said:—"I have often tried, as Mr. Josiah Cooke has on his part, to compare them, to combine them, and to discuss them, with the hope of drawing some conclusion from them with certainty, but I have been unable to draw from them anything but doubt. The formula deduced from the above simple progression" $(a+n\,d)$ "would not account for the generation of simple bodies, as Cooke had supposed; but organic radicles are not always formed by addition, they are also produced by substitution, as we see in the compound ammoniums." Dumas proposed to substitute a formula like $n\ a+n'\,d+n''\,d'$; a being the nucleus, d and d' the common differences, and n, n', n'' whole numbers. Table IV. shows the series of Cooke and Dumas.

Following in their footsteps, Professor Newlands extended their principles to include newly discovered elements. Employing Cannizzaro's atomic weights instead of those of the old system, and collating his own results and all discovered up to 1864, he arranged the groups in horizontal lines instead of vertical columns, and then discovered the "Law of Octaves," as shown in Table IV. The coincidence of the ordinal numbers led him, in 1865, to express the following opinion:—"I will endeavour to show that all the numerical relations among the equivalents pointed out by M. Dumas and others, including the well-known triads, are merely arithmetical results flowing from the existence of the 'law of octaves,' taken in connection with the fact of the equivalents forming a series of numbers approaching to the natural order." And in 1866: "The fact that such a simple relation exists now affords a strong presumptive proof that it will always continue to exist, even should hundreds of new elements be discovered. For, although the difference in the numbers of analogous elements might, in that case, be altered from 7, or a multiple of 7, to 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the number of analogous elements would be none the less evident."* The law of regular increase, however, points to a relationship far more significant than the identity of their ordinal numbers.

Working independently of Newlands, Mendeleeff discovered the periodic law in 1869. It has offered a grand incentive to new discoveries and received well-merited recognition throughout the world. The extracts from Wurtz and Meyer, at the beginning of this paper, show what it left to be desired.

A paper by Rev. Dr. Haughton, and an abstract of one by Mr. Stoney, have recently appeared in the Chemical News. Each gives a clear enunciation of the nature of the problem. Dr. Haughton discovers some of the regular intervals noticed here. Unfortunately, the paper of Stoney, on "The Logarithmic Law of Atomic Weights,"† is so abridged that it is hard to determine how his results may compare with those herein discussed. The abstract states that, in plotting the atomic volumes as ordinates of a diagram, the effort to extract information from the resulting curves was a failure; in plotting their cube roots, however, he found a logarithmic curve with perturbations which showed a distinct law of increase for perissads and artiads. The abstract was not discovered until most of this paper was written, and, from its indefinite statements, it would require much time to construct the curves and divine the inferences.

At the close of his paper of 1854, Professor Cooke said:—"To my conceptions chemistry will then have become a perfect science, when all substances have been classed in series of homologues, and when we can make a table which shall contain, not only every known substance, but also every possible one, and when by means of a few general formulæ we shall be able to express all the properties of matter, so that when the series of a substance and its place in the series are given we shall be able to calculate, nay predict, its properties with absolute certainty. . . . Then the dreams of the ancient alchemist will be realised, for the problem of the transmutation of metals will have been theoretically, if not practically, solved."

* *Comptes Rendus*, 1857, p. 709.

* The "Periodic Law," p. 20.

† Chemical News, vol. lvii., p. 163.

TABLE III.—*Deviations.*

Grm. Ser.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	−0·03	?	−0·03	0·00	?	−0·01	−0·03	
2	−0·02	−0·02	−0·00	+0·02	−0·08	+0·01	+0·32	
3	−0·02	−0·08	?	0·00	+0·05	+0·19	(−0·26)	−0·11
4	+0·06	?	−0·30	?	−0·06	+0·03	+0·01	
5	+0·64	+0·28	+0·01	−0·80	−0·30	+0·47		+0·02
6	+0·08	+0·03	−0·36	−0·42	−0·14	+0·31	+0·41	
7	+0·25	+0·02	−0·18	?	−0·05			
	+0·14	+0·05	−0·14	−0·25	−0·09	+0·17	+0·18	−0·05

Electro chemical Order.

1	5	?	49	48	?	63	60	
2	4	9	13	42	55	62	59	
3	3	8	?	43	52	53	(19)	21
4	31	20	?	?	54	56	58	
5	2	7	11	14	44	51		34
6	32	24	27	28	47	46	57	
7	1	6	18	16	17			

TABLE IV.

COOKE, 1854.

Ser.	III.			IV.		V.	VI.	VIII.	IX.	IV.		
Gr.	3.	2.	1.	3, 2.	1.					2.	1.	3.
	H	Ca	Mg	Al	Ti	C	O	O	O	Al	Ti	Cu
	Li	Sr	Zn	Cr	Pd	B	N	S	F	Cr	Pd	Hg
	Na	Ba	Cd	Mn	Sn	Si	P	Se	Cy	Mn	Sn	
	K	Pb		Fe	Pt		As	Mo	Cl	Fe	Pt	
	Ag			Co	Ir		Sb	Te	Br	Co	Ir	
				Ni	Os		Bi	V	I	Ni	Os	
				U	Au			W		U	Au	
				Cu				Ta				
				Hg								
	Cu	Mn				Ti	Cr	As	Cr			
							V	Mn	Mn			
									Os			
									Au			

DUMAS, 1857.

Form.	7+*n* 8.	12+*n* 8.	25+*n* 34.	6+*n* 5.	14+*n* 17.	8+*n* 8.	19+*n* 16·5+*n*′ 28.
	L	Mg	Ti	C	N	Cr O	F
	Na	Ca	Sn	B	P	Mo S	Cl
	K	Sr	Ta	Si	As	V Se	Br
		Ba		Zr	Sb	W Te	I
		Pb			Bi		

MENDELEEFF, 1869.

Gr. Ser.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni Cu
5	(Cu)	Zn	Ga	—	As	Se	Br	
6	Rb	Sr	? Y	Zr	Nb	Mo	—	Ru Rh Pd Ag
7	(Ag)	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	? Di	? Ce				
9	(—)							
10			? Er	? La	Ta	W		Os Ir Pt Au
11	(Au)	Hg	Ti	Pb	Bi			
12				Th		U		

NEWLANDS, 1865.

No.		No.		No.		No.		No.		No.		No.	
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
G	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba & V	45	Pb	54
Bo	4	Al	11	Cr	19	Y	24	Ce & La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Os	51

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 173).

PROBLEM III. *To Separate the Active from the Inactive Constituent of Air.*—It now has become of importance to get this active constituent of the air by itself, and the question arises whether it cannot be separated from one of the metals or other substances with which it has been found to combine. The pupil is therefore told to collect information about the different substances formed by burning metals, &c.—whether they can be obtained in sufficient quantity to work with, &c. Iron rust and iron scale are easily obtainable, and so is copper scale; zinc is burnt to produce zinc-white, which is used as paint; lead is also burnt on a large scale, and in this case it appears that one or other of two substances is formed—litharge at a high temperature, red lead at a lower temperature. This peculiarity of lead suggests the study of the two products in the hope of discovering the clue to a method. Weighed quantities of the litharge and red lead are heated; it is observed that only the latter changes in appearance and that it loses weight. But what does it lose? It was formed by merely roasting lead in the air, and the something which it loses must therefore have been derived from the air. If the red lead is heated in a tube a gas is given off which is collected and tested—how? with a taper or glowing splinter as it is to be supposed that the gas will support combustion if, as is to be expected, it is the active constituent of air. The *discovery* of the active constituent of air is thus made! If air consist of this gas and that which remains after exposing phosphorus or iron in air, then by adding to such residual air as much of the gas from red lead as was withdrawn, air should be re-obtained; this is found to be the case. The names of the two gases are now *for the first time* stated, and an easy method of preparing oxygen is demonstrated, such as that of heating chlorate, but without any explanation. The conclusion previously arrived at, that probably in all the cases previously studied of changes occurring in air, the oxygen is the active substance, may now be verified by burning or heating in oxygen the substances which had been burnt in air.

So much having been learnt of the chemistry of air, the study of the pressure exercised by air may next be taken up, and the common pump, the force pump, the barometer and air currents may be discussed and explained. Now-a-days the charts given in the daily papers, and the Ben Nevis and Glycerin barometer readings quoted in the *Times* make it particularly easy to explain the barometer. The pupils should be led to make barometer curves.

PROBLEM IV. *To Determine the Composition of Chalk.*—The discovery of the *composition* of the air in the course of experiments made with the object of determining the nature of certain changes naturally suggests that the attempt be made to ascertain the composition of other things by studying the changes which they undergo. Chalk is known to give lime when burnt, and experiments made in Stage III. have indicated that chalk loses something when burnt—the idea that an invisible something is given off is especially probable after the experiments with red lead have been made; so it is decided to heat chalk strongly, but before doing this chalk and lime are examined comparatively. Chalk is not observed to be altered by water; on shaking it up with distilled water and evaporating some of the filtered liquid in a weighed dish, very little residue is obtained—so it is established that it is but very slightly soluble in water. Lime is slaked, weighed quantities of lime and water being used; the retention of a considerable amount of water, even after exposing the slaked lime in the drying oven, shows that the slaking involves a definite change in composition—that slaked lime is lime and water. The solubility of the lime is next determined, and found to be considerably greater than that of the chalk. It is found that chalk is but very slightly altered in weight when heated over a gas flame, and that it is only when it is strongly heated that it is converted into lime: so the chalk is strongly heated in an iron tube in a Fletcher blowpipe furnace, when gas is freely given off. This is tested with a taper, which it extinguishes, so it cannot be oxygen, but may be nitrogen; if it be nitrogen, when mixed with oxygen in the proportion of 1 to 4, it should give air, but this is found not to be the case; so evidently it is a peculiar gas, and may be called chalk gas. If chalk consist of this gas and lime it should be possible to reproduce chalk from them; so the gas is passed through a small weighed tube containing lime and the tube is found to get heavier. But lime and chalk are so much alike that it is difficult to say that chalk is formed; perhaps dissolved lime will act similarly; the gas is therefore passed into or shaken up with lime water. The precipitate which forms looks like chalk, and probably is, but this remains to be decided. The discovery of this behaviour of chalk gas, however, is important as affording a means of again comparing the gas from chalk with nitrogen. In working with lime water it is scarcely possible to avoid noticing that a film forms on its surface; by exposing a quantity of the lime water a considerable amount of the precipitate is obtained; its resemblance to chalk is noted, and the possible presence of chalk gas in air is thus suggested; but in view of the absence of proof of the identity of the precipitates with chalk a decision is reserved. The discovery is made, however, that air contains something besides oxygen and nitrogen.

It being thus established that chalk consists of two things, lime and chalk gas, at this stage it is pointed out how firmly these two constituents hold to each other in the chalk. The absorption of the gas by the lime—its entire disappearance in fact—is commented on. Accurate determinations of the loss of weight on heating crystallised chalk (calc spar) should at this stage be carried out before the class, if not by the pupils, so that the numbers may be quoted and that it may become impressed on them that the proportions in which the lime and chalk gas are present is constant. Their attention may be recalled to the oxides previously studied, it being pointed out that on inspection these afford no indication that they contain oxygen: that here again the gas entirely loses its individuality on entering into union or combining. That oxides contain their constituents in fixed proportions may be demonstrated experimentally by oxidising finely-divided copper and determining the increase in weight, lime being used as drying agent. In this way the characteristics of *compounds* are elucidated. Then the comparison may be made with air and the fact made clear that it behaves as a mere mixture. Still no reference should be made to elements.

PROBLEM V. *To Determine what Happens when Organic Substances are Burnt.*—The experiments thus far made have shown that phosphorus and a number of metals burn in the air because they combine with the oxygen, forming oxides, heat being given out *as a consequence*; but that chalk when burnt is split up or decomposed into lime and chalk gas, this result being a consequence of the heating alone, the air having nothing to do with it. It remains to ascertain what happens when organic substances are burnt, as these give no visible product beyond a little ashes. As in all cases when vegetable or animal substances are burnt a certain amount of "char" is obtained, which then gradually burns away, charcoal or coke is first studied. It having been discovered that the oxygen in air is the active cause of burning in many cases, it appears probable that the air is concerned in the burning of

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

charcoal, coal, &c. As when once set fire to these continue to burn, the charcoal is at once heated in oxygen: it burns, but no visible product is formed: it therefore follows that if the charcoal is oxidised the oxide must be an invisible gas. How is this to be tested for? What gases are already known to the pupil? How are these distinguished? Oxygen is excluded. Is it perhaps nitrogen, and is not perhaps the nitrogen in air merely used-up oxygen as it were, produced by the burning of organic substances? Or is it perhaps that gas which was found in the air along with oxygen and nitrogen, and which turned lime water turbid? This last being an easy test to apply is at once tried; the lime water is rendered turbid, and so to leave no doubt a sufficient amount of the gas is prepared and passed into lime water, the precipitate is collected, and the loss it suffers on heating is determined and found to agree with that suffered by the precipitate prepared from chalk gas. Finally, to ascertain whether the product is really heavier than the charcoal burnt, as in the case of the metals previously studied, the charcoal is burnt in oxygen in a tube connected to a flask containing milk of lime with a lime-drying tube attached to it; the tube is weighed before and after burning. Thus the discovery is made that chalk gas is an oxide of carbon, and that chalk consists of at least three things.

It may be objected that to make the experiment in this manner takes too much time; but to this it may be answered that such experiments are precisely of the kind of those made in actual practice, and that they exercise a most important influence in teaching the pupils to take nothing for granted, never to jump at conclusions, and to rest satisfied if they progress surely, however slow the advance may be.

A number of organic substances may now be burnt, and the gas passed into lime water; chalk gas is found in every case to be a product, and hence the presence of a common constituent—carbon in all is established. In making these experiments the formation of a liquid product is observed, so it is evident that chalk gas is not the only product, or carbon their only constituent.

Food materials generally having been found to contain "carbon," as they are obviously in some way destroyed within the body, and it is known that air is necessary for life, the question arises, what becomes of food, and why is air necessary for life? Is the food, perhaps, in large part "burnt up" within the body, thus accounting for the fact that our bodies are always warm? The characteristic product of combustion of carbonaceous substances is therefore tested for by breathing into lime-water. The discovery thus made affords an opportunity for a digression and for explaining how plants derive their carbon from the air.

Problem VI. *To Determine what Happens when Sulphur is Burnt.*—From the results of the experiments with carbon, it appears probable that the disappearance of sulphur when burnt is also really due to its conversion into a gaseous oxide, so it is kindled and introduced into oxygen: if it be burnt over water in a bell jar in a spoon passing through the stopper (a rubber cork), the water is seen to rise; if, on the other hand, it be burnt in a dry flask closed by a rubber cork carrying a guage-tube, as suggested by Hofmann,* the volume is seen to be almost unchanged after combustion. It follows, therefore, that the sulphur and oxygen unite and form a soluble product. Sulphur is next burnt in a tube in a current of oxygen, and the gas is passed into water; a solution is thus obtained having the odour of the gas and sour (acid) to the taste. The fact that carbon and sulphur—both non-metals—behave alike in yielding gaseous oxides suggests that a comparison be made of their oxides: so the acid solution is added to lime water; a precipitate is formed which re-dissolves on adding more of the sulphur gas solution; on the other hand, on adding the lime water to the acid liquid, this latter after a time loses its characteristic smell. There can be no doubt, therefore, that the sulphur gas does in some way act upon the lime. The experiment is then made of burning the sulphur in a weighed tube containing lime; the weight increases, so that no doubt remains that sulphur, like carbon, forms an oxide when burnt. The discovery that the addition of more of the sulphur oxide leads to the dissolution of the precipitate which it first forms in lime water, suggests trying the effect of excess of the carbon oxide on the lime water precipitate; this is done, and the discovery is made that the precipitate gradually dissolves. The solubility of the new substance may then be determined by passing the gas into water containing chalk in suspension, filtering, and evaporating. This leads to the observation that a precipitate is formed on heating the liquid, and this is soon found to be chalk. An opportunity is thus afforded of explaining the presence of so much "chalk" in water; of demonstrating its removal by boiling and by lime water; and the effect it has on soap.

The observation that the oxides of both carbon and sulphur combine with lime suggests trying whether the one will turn out the other, so the solution of the sulphur oxide is poured on to chalk; effervescence is observed, and on passing the gas into lime water a precipitate is obtained. The production of this effect by the *acid* solution suggests trying common vinegar—a well-known *acid* substance. This also is found to liberate chalk gas, and the discovery of an easy method of preparing chalk gas is thus made. The oxide formed on burning phosphorus, having previously been found to give an acid solution, is tried, and it is found that it also liberates chalk gas. As a good deal of vinegar is found to give very little chalk gas, the question arises, Are there not acids to be bought which will have the same effect and are stronger and cheaper; On inquiry it is found that sulphuric acid or oil of vitriol, muriatic acid or spirits of salts, and nitric acid or aquafortis may be bought, and that these all act on chalk. The behaviour of chalk with acids affords a means of testing the lime water precipitate obtained in working out Problems IV. and V. In this manner the pupil is led to realise that certain agents may very readily produce effects which are only with difficulty produced by heating—that the *chemical agent* may produce very powerful effects. The ready expulsion of the carbon oxide of the chalk suggests that other substances not yet studied, such as the metals, when treated with acids may behave in a special manner which will afford information as to their nature. At this point, prior to making the experiments with the acids, an explanation may be given of the names *oil of vitriol*, *spirits of salts*, and *aquafortis*; the processes by which they are made may be described and illustrated, without, however, any attempt being made to explain them from the chemical point of view. The sulphuric acid should be made from green vitriol, and its behaviour on dilution should be demonstrated as well as its use as a drying agent.

Problem VII. *To Determine what Happens when Metals are Heated with Acids.*—Iron, zinc, lead, tin, copper, and silver may be taken. On pouring diluted oil of vitriol on to iron or zinc, the metal dissolves with effervescence; the gas is collected, and, when tested, is found to burn. Thus, a new gas is discovered, differing from all which have previously been studied, inasmuch as it is combustible; in order not to interrupt the study of the action of acids on metals, however, its further examination is postponed for a while. Resuming the experiments with metals, lead, tin, copper, and silver are found not to be acted upon by diluted oil of vitriol.

Muriatic acid, in like manner, dissolves iron and zinc and also tin with effervescence, and the gas which is given off in each case exhibits the same behaviour as that

* By burning carbon also in this way a most effective demonstration is given of the fact that no loss or gain of matter attends the change, and that only heat escapes; the results in the case of carbon and sulphur are particularly striking, as the products are gaseous and invisible.

obtained from iron or zinc and diluted oil of vitriol. Lead, copper, and silver are not appreciably affected.

Aquafortis is found to dissolve not only iron and zinc but also copper, lead, and silver, and to convert tin into a white substance—to attack all the metals in fact, thus justifying its name. The gas which is given off as the metal dissolves is observed to be coloured; when it is collected over water, however, it is seen to be colourless, and to become coloured on coming into contact with air—oxygen and nitrogen are, therefore, added to portions of the gas over water. In this manner not only is a new gas discovered, but also a test for oxygen; and opportunity is afforded of here calling attention to the fact that air behaves exactly as oxygen, that the oxygen in air appears to be unaffected by its association with nitrogen—that, in fact, it is uncombined. From these experiments it is obvious that metals and acids interact in a variety of ways. Finally, the dissolution of gold and platinum by aqua regia may be demonstrated.

Problem VIII. *To Determine what Happens when Oxides are Treated with Acids.*—In the course of the previous experiments a number of oxides have been prepared by burning various metals in air; these are found to be unchanged by water. The discovery that acids act on metals suggests a trial of the effect which acids will have on their oxides; so the oxides of zinc, iron, copper, and lead are submitted to the action of the three acids previously used. Sulphuric acid is found to dissolve zinc oxide, iron rust, and copper oxide, but no gas is evolved; excess of the oxide may be used, and the filtered liquid concentrated; the crystals which separate may be examined and compared with those obtained by dissolving the metal in sulphuric acid, &c. Litharge apparently is not changed by sulphuric acid, but red lead is, although not dissolved. Muriatic acid being used, all the oxides are found to dissolve, and in the case of red lead a greenish yellow gas is given off, possessing a most disagreeable smell; this is noted as a case for study. The product from the lead oxides is observed to crystallise out from the hot liquid on standing, so the undissolved original product is boiled up with water and the solution is filtered, &c. Attention is thus directed to the difference in solubility of the products. Next, aquafortis is used; again, all are dissolved, except the red lead, which, however, is obviously altered. In the case of the lead oxides the product is again less soluble than those afforded by the other oxides, but more soluble than the product obtained on using muriatic acid. The pupil has already been led to realise that of two substances capable of acting on a third, such as chalk gas and sulphur gas, which both combine with lime, one may be the stronger, and may turn out the other, sulphur gas turning out chalk gas from chalk. A comparison of the three acids with the object of ascertaining which is the strongest is therefore suggested—the metal or oxide is dissolved in one of the acids, and the others are then added. No positive result is obtained in the case of zinc, iron, or copper, but the solution of lead in nitric acid is precipitated by muriatic and by sulphuric acid; the former precipitate is found to dissolve in boiling water and to crystallise out in exactly the same way as the substance obtained from lead oxide and muriatic acid. The sulphuric acid product is found to be almost insoluble in water, and also in muriatic and nitric acids; these observations make it possible, by examining the behaviour towards muriatic and nitric acids of the products of the action of sulphuric acid on the lead oxides, to establish the fact that the product is the same whether lead be dissolved in nitric acid and sulphuric acid be then added, or whether either of the oxides be treated with sulphuric acid. It is further evident that those acids which give difficultly soluble or insoluble products act with difficulty, if at all, on the metal. Other metals besides those mentioned may be now studied, and, a solvent being found, the acids which do not dissolve the metal may be added to the solution. In this way, for example, the chloride test for silver is discovered.

In experimenting with acids the pupils can hardly fail to stain their clothes and their fingers. The observation that acids alter colours serves to suggest experiments on the action of acids on colours, especially those of leaves and flowers. The use of litmus, methyl orange, cochineal, &c., may then be explained. As various oxides have been found to "neutralise" acids, the study of their effect on the colours altered by acids is suggested. Lastly, a few experiments with vegetable and animal substances, sugar, &c., may be made, which demonstrate the corrosive action of oil of vitriol and aquafortis.

Problem IX. *To Determine what Happens when the Gas obtained by Dissolving Iron or Zinc in Sulphuric or Muriatic Acid is Burnt.*—The gas has been observed to burn with a smokeless odourless flame. To ascertain whether, as in all other cases of combustion previously studied, the oxygen of the air is concerned in the combustion, a burning jet of the gas is plunged into a dry cylinder full of oxygen, in which it is not only seen to continue burning, but it is also noticed that drops of liquid condense on the cylinder above the flame; this immediately suggests that the product is a liquid. The jet is found to be extinguished in nitrogen, so evidently when the gas burns it forms an oxide. The experiment is repeated and the gas burnt in a bell jar full of oxygen over water; the water rises as the combustion proceeds, proving that the oxygen is used up. To collect a sufficient quantity of the product for examination the dried* gas is burnt at a jet underneath a Florence flask through which a stream of cold water is allowed to circulate: the neck of the flask is passed through the neck of a bell jar and the flask and bell jar are clamped up in an inclined position, so that the liquid which condenses may drop into a small beaker placed below the rim of the jar. What is the liquid? It looks very like water, and is without taste or smell. Is it water? How is this to be ascertained? What are the properties of water? The knowledge previously gained here becomes of importance. It has been observed that frozen water melts at 0° Centigrade, that water boils at 100°, and that 1 c.c. weighs 1 grm. at 4° C.; so the liquid is frozen by the ice-maker's mixture of ice and salt, a thermometer being plunged into it so that the solid ice forms on the bulb; the melting-point is then observed. Subsequently the boiling-point is determined, a little cotton-wool being wrapped around the bulb of the thermometer. Lastly, the density of the liquid may be determined. It is thus established that the gas yields water when burnt, and the name of the gas may now, *for the first time*, be mentioned and explained. The results thus obtained leave little doubt that water is an oxide of hydrogen; but in order to place this beyond doubt it is necessary to exclude nitrogen altogether. How is this to be done? Red lead is known to consist of lead and oxygen only, and readily parts with a portion, at least, of its oxygen; so dried oxygen is passed over red lead, which is then gently heated. Again a liquid is obtained which behaves as water, so there can be no doubt that water is an oxide of hydrogen. Water is not obtained on merely mixing oxygen and hydrogen; it is only produced when combustion takes place. To start the combustion a flame is applied to a small quantity of a mixture of the two gases: a violent explosion takes place. An opportunity is here again afforded of calling attention to the entire change in properties which takes place when the compound is formed. On heating red lead in hydrogen, lead is obtained, although on heating it alone it loses only a portion of its oxygen, and the "reduction" takes place very readily; evidently, therefore, hydrogen is a powerful agent. This observation suggests further experiments. Will it not be possible to remove oxygen by means of hydrogen from other oxides which are not altered on heating? and will not

* The importance of drying the gas is realised without difficulty, as previous observations have shown that the air is moist, and, as the gas is given off in presence of water, lime may be used.

other combustible substances besides hydrogen remove oxygen from oxides?

PROBLEM X. *To Determine what Happens when Hydrogen and other Combustible Substances are Heated with Oxides.*—Zinc oxide, iron rust, and copper oxide are now heated in a current of hydrogen: the first remains unaltered, the other two are seen to change, a liquid being formed which it cannot be doubted is water; the copper oxide evidently becomes reduced to copper. Is the iron rust similarly reduced to the metallic state? How is iron to be tested for? Iron is attracted by the magnet, and dissolves in diluted oil of vitriol with evolution of hydrogen. Applying these tests, no doubt remains that the iron rust is deprived of its oxygen.

Litharge and copper oxide may then be mixed with soot or finely-powdered charcoal and heated in tubes; gas is given off which renders lime-water turbid, and metallic lead or copper is obviously obtained. It is thus established that some, but not all, oxides may be deprived of their oxygen by means either of hydrogen or carbon. Opportunity is here afforded of explaining the manufacture of iron.

Several dried combustible organic substances, sugar, bread, and meat, may now be burnt with copper oxide in a tube, the fore part of which is clean and is kept cool: liquid is seen to condense, while "chalk-gas" is given off; the liquid has the appearance of water, and sufficient may easily be obtained to ascertain whether it is water. The presence of hydrogen in organic substances is thus discovered; its origin from water may now be explained, and the double function of water in the plant and animal economy may be referred to—viz., that it both enters into the composition of the animal and plant structure, and also acts as a solvent. The combustion of ordinary coal-gas, of alcohol, of petroleum, of oil, and of candles, may then be studied, and the presence of hydrogen in all of these noted.

(To be continued).

CORRESPONDENCE.

THE AMINES SEWAGE PROCESS.

To the Editor of the Chemical News.

SIR,—Having recently attended a demonstration of the above process at the Wimbledon works, on the occasion of a meeting of the members of the Society of Municipal Engineers, I read your communication (CHEMICAL NEWS, vol. lx., p. 157) with interest.

We are accustomed to see extravagant accounts of the marvellous effects of "chemicals" in the columns of Dailies; but the minds of chemists are not so easily disturbed, and it is in your columns, "par excellence," that the real grit of an invention should be ground out. With that object in view I venture to make some comments upon this process.

You say the process you witnessed was as follows:—

"Milk of lime was mixed in the proportion of about 4½ lbs. per 1000 gallons, along with about 18 ozs. of trimethylamine. It does not sufficiently appear whether these 18 ozs. are to be actual trimethylamine or brine, &c., in which such a quantity of trimethylamine has been found to be present."

Herr Wolheim stated at Wimbledon that herring-brine contained two-thirds of a percentage of trimethylamine. That being so, to obtain 18 ozs. of trimethylamine we should need 2727 ozs. of the brine. If the 18 ozs. are to be read as meaning brine, these 18 ozs. of a two-third's per cent solution would contain 0·118, or just over $\frac{1}{10}$ oz. of trimethylamine for each 1000 gallons of sewage, or 0·051 grains per gallon. Say we have a flow of three millions of gallons of sewage, and that the 18 ozs. are trimethylamine, then about 50,000 gallons of brine would be used up daily.

Here we have the horns of a dilemma, and I should like to know upon which horn Herr H. Wolheim prefers to rest.

That Dr. Klein found an effluent after treatment with between 70 and 80 grains per gallon of lime to be sterile does not appear to me to be remarkable, and, of course, if it be sterile from its alkalinity it would not decompose upon keeping.

I should almost as much expect to find living organisms in, say, sulphuric acid as in such an alkaline liquid.

In such an effluent there would be much putrescible matter in solution, and if the fluid were diluted with ten times the bulk of ordinary river water, with its usual microbian populations, fermentative changes would most likely be set up. It is like passing through a second period of juvenility to be fighting the old lime fallacy; a ghost long since laid has again raised its head, but this time *Cum grano salis*.—I am, &c.,

CYCLOPS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 10, September 9, 1889.

The Fixation of Atmospheric Nitrogen.—M. Berthelot.—The author holds that the opinion that the free nitrogen of the atmosphere plays no part in vegetation or in agriculture has been abandoned, except, possibly, by M. Schlœsing, who does not express himself decidedly upon this point. This change of views M. Berthelot ascribes to the researches which he has carried on for the last six years, and which have led to other investigations, such as those of G. Ville, of MM. Hellriegel and Willfarth, of M. Dehérain, and M. Joulie, &c. The active agents in the fixation of nitrogen he considers to be certain microbia. The causes why, in some experiments, the results obtained have been negative may be the exposure of the soil to the deleterious vapour of mercury, or the application of a heat sufficient to kill the microbia, or operating on soils already saturated with nitrogen.

Observations on the Formation of Ammonia and of Volatile Nitrogenous Compounds at the Expense of the Vegetable Mould and of Plants.—M. Berthelot.—Vegetation is constantly attended by an exhalation of ammonia and of other volatile compounds. This exhalation, though very trifling, deserves attention, because the volatile nitrogenous compounds emitted by living beings are often possessed of an extremely active poisonous property, even as regards the very living beings by which these compounds have been secreted.

The Nitrification of Ammonia.—Th. Schlœsing.—The nitrification of the ammonia applied to a hectare of land may be very rapidly accomplished when it is favoured by the nature of the soil, its humidity, and its temperature. In a future communication the author proposes to examine the case when the ammonia is applied in the free state or as carbonate in too large a quantity, when it becomes injurious to the nitric ferment.

The Spectrophotography of the Invisible Parts of the Solar Spectrum.—Ch. V. Zenger.—A single prism of rock-salt, combined with two prisms of anethole increase the dispersion ninefold, and the red part of the

spectrum is six times more dispersed between A and D than by a prism of rock-salt.

Researches on the Sulphites.—P. J. Hartog.—The author describes the sodium-ammonium sulphite-bisulphite, a compound obtained by passing a current of gaseous ammonia into a saturated solution of sodium bisulphite. He also describes an isomeric modification of sodium metasulphite.

A New Monobromated Camphor. On the Constitution of the Monosubstituted Derivatives of Camphor.—P. Cazeneuve.—The mono-bromo- substitution compound presents similar properties to the chloro-derivative obtained by means of hypochlorous acid. The bromine has been substituted for hydrogen in a CH_2 of the nucleus.

On Phenol-disulphonic Acid.—J. Allain Le Canu.—The author has obtained this compound by placing sulphuric acid of sp. gr. 1·84 and pure phenol over each other in a bell exhausted of air.

Influence of Gypsum and Clay on the Preservation of Nitrogen, the Fixation of Atmospheric Nitrogen, and Nitrification.—M. Péchard.—The addition of baked gypsum to sandy soils containing nitrogen greatly reduces the loss of nitrogen. Clay was found to have a similar effect.

Manufacture of Red Glass for Windows.—Ch. Guignet and L. Magne.—The authors have studied the composition of old coloured glasses of the twelfth and thirteenth centuries. They give diagrams showing the structure of some specimens.

No. 13, September 23, 1889.

This number contains no chemical matter.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 1.

New Apparatus for the Concentration of Extracts in a Vacuum.—L. A. Adrian.—This paper cannot be reproduced without the two accompanying plates.

On the Sulphur Compounds of the Cruciferæ.—W. J. Smith (*Annales Agronom.*).—To determine the myronic acid the quantity of sulphuric acid pre-existing in the seeds before the myronate is split up must be determined. To this end the action of the ferments contained in the seeds must be arrested by treating them with hydrochloric acid at 0·3 per cent. The author has operated on the seeds of black mustard, determining the sulphur present in the state of sulphuric acid, and then the total sulphur. Rather more than one-third of the total sulphur belongs to the albumenoids and the rest to the myronic acid.

House Filters and Potable Waters.—A. J. Snijers (*Deutsch. Med. Wochenschrift*).—The author states that fine sea-sand, washed and raised to a high temperature, arrests almost all the organic germs and bacteria. He compares in this respect (removal of living organism) the value of the filters of Pasteur, Chamberland, and of Maignen. The former retains its sterilising power for at least two months, but its action upon the chemical impurities is slight. Without pressure the filtration is too slow, scarcely a litre an hour. The Maignen filter has less action on bacteria, and loses its sterilising power in a few days. It yields 40 litres in twenty-four hours. The filtrate contains one-half less solids than the original water, the organic matter disappearing almost entirely. The action is perfect for salts of lead and iron, good for nitrates and ammonia, null for chlorides.

Separation of Strychnine and Brucine.—J. E. Gerock (*Archive der Pharm.*).—The alkaloids are precipitated in heat from their neutral solution by picric acid. The mixture is let cool, and, after being let stand for a sufficient time, the picrates are thrown upon a tared filter, washed in cold water until the liquid runs through colourless, dried at 105°, and weighed. As much as possible of the precipitate is removed from the paper and put in a beaker. On the other hand, the filter is repeatedly washed with nitric acid of sp. gr. 1·056 previously heated in the water-bath. The brucine picrate which remained adhering to the paper is thus destroyed. The nitric acid is then poured upon the precipitate previously removed, and it is heated on the water-bath for some time. It is then exactly neutralised, a trace of acetic acid is added (strychnine picrate, though soluble in nitric acid and in the alkalies, is insoluble in dilute acetic acid), and it is let cool. Lastly, the strychnine picrate is thrown on the filter already used, washed, dried, and weighed. The difference of the two weights shows the quantity of brucine present in the mixture.

A New Salt bordering on Potassium Ferrocyanide.—F. Mahla (*Berichte*).—If we exhaust with cold water the mixture which has served for purifying coal-gas and submit the liquid to fractionated precipitation with ferric chloride, the last portions, instead of prussian blue, yield a deep violet precipitate. This precipitate, if treated with alkalies, yields ferric oxide, and a yellow solution which, after neutralisation, gives, with ferric chloride, a violet precipitate, with copper salts a parrot green, and with salts of cobalt a fresh red.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Parts 3 and 4.

Experimental and Theoretic Study on the Conditions of Equilibrium among the Solid and Liquid Combinations of Water with Salts, especially with Calcium Chloride.—H. W. Bakhuis Roozeboom.—This memoir, which extends to 150 pages, discusses in succession the various hydrates of calcium chloride and their solubilities, the general solubility of salts, the phenomenon of supersaturation, and the condition of salts in a saturated solution; the tension of the different systems composed of calcium chloride and water; the conditions of equilibrium of these systems; the thermo-dynamic relations for the vapour-tensions of the different systems of water and of a salt; application to the case of calcium chloride and a general review of other salts; and lastly, thermo-dynamic relations for the concentration of solutions in equilibrium with a solid salt and vapour of water.

NOTES AND QUERIES.

***** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.**

Separation of Sulphides.—We are directed in most works on qualitative analysis in the H_2S group, for the separation of the sulphides of As, Sb, and Sn from Hg, Cu, Pb, Bi, and Cd, to digest the precipitate in $(H_4N)_2S$ (yellow), in which As, Sb, and Sn are soluble, while the others are not so (or only slightly, as Cu). As, after repeated trials, I have never yet had good success in this stage of the analysis, I would be obliged to any chemist who has worked it satisfactorily for the *minor details* of the process, including directions for making the $(H_4N)_2S$ as used by him in it.—P. D.

Molecular Volumes.—Can any of your readers give me any information as to the recent experiments mentioned in the following question, taken from a chemistry examination paper? "The molecular formulæ of the elements are generally taken as representing two volumes of gas: thus H_2 is said to represent two volumes of hydrogen, while the elementary symbol H is taken as the unit associated with the idea of one volume. Show from recent experiments that this is inadmissible, and that the gaseous atom cannot be supposed to occupy one volume."—STUMPED.

TO CORRESPONDENTS.

Ibn. Menenek.—Reference to the indices of our back volumes will give the desired information.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation, of Berlin, in the Empire of Germany, has applied for leave to amend the Specification of Letters Patent No. 4415 of 1884, granted to Gerard Wenzeslaus von Nawrocki for "Improvements in the manufacture of colouring matters."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 2nd October, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
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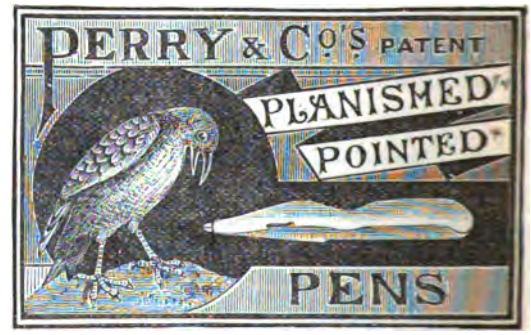

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THE CHEMICAL NEWS.

Vol. LX. No. 1560.

A WATER-JACKETTED FLEXIBLE TUBE.

By FREDERICK J. SMITH.

It is often convenient to conduct gases through flexible tubes, but the convenience is not without its disadvantage, since some gases diffuse readily through rubber. Having to deal with electrolytic gas in a research on explosions in tubes, and believing that some error would be introduced by the use of rubber tubes as usually employed, I devised a flexible tube almost quite free from the disadvantage mentioned. As the device may possibly be of use in the laboratory, I venture to send a description of it to the Chemical News.

A length of small rubber tube is drawn through another tube of equal length but of greater diameter; each end is furnished with a small length of glass tube fitting the smaller tube; one end is bound off with cord, then the space between the inner and outer tube is filled with water or any liquid required; the other end is then bound off. By this means a water-jacketted flexible tube is easily constructed.

Millard Laboratory, Trinity College,
Oxford, October 8, 1889.

ON THE REACTION OF BENZOQUINONE WITH POTASSIUM CYANIDE.*

By S. A. SWORN, B.A., Assoc. R.C.Sc.L.

Hydrocyanic acid does not form a compound with benzoquinone. The latter body, however, readily combines with potassium cyanide to form a dark green body, which is obtainable only in aqueous solution. One molecule of the quinone combines with one of the cyanide. Anthraquinone does not form such a compound. Hydrocyanic acid (but no quinone) is given off when the solution is boiled, and quinone is liberated by the addition of silver nitrate solution.

CONTRIBUTIONS TO THE STUDY OF PURE FERMENTATIONS.*

By Professor PERCY F. FRANKLAND, Ph.D., B.Sc.
GRACE C. FRANKLAND, and J. J. FOX.

The authors point out how very few of the bacterial fermentations hitherto studied have been performed with ferments of undoubted purity, as well as the insufficiency of the description of the morphological characters of the organisms in question. Such scanty descriptions generally render it impossible for other investigators to know whether they are dealing with the same or with different ferments.

The authors have isolated and fully characterised by the modern methods of cultivation an organism, a small bacillus, which sets up fermentation not only in solutions of glucose cane-sugar, milk-sugar, and starch, but also in solutions of mannite, glycerin, and calcium glycerate. The fermentations of mannite and glycerin have alone been so far studied.

In each case the products are essentially the same, viz., principally ethyl, alcohol, and acetic acid, together with smaller quantities of formic acid and a trace of succinic acid. The alcohol was separated by distillation and the quantity determined, whilst the several acids were estimated by conversion into their barium salts in the case of the acetic and formic acids, whilst the succinic acid was extracted and weighed in the free state.

In the case of the mannite fermentations it was found that the amount of alcohol and acetic acid formed stood in the proportion of two molecules of alcohol to one molecule of acetic acid, whilst in the glycerin fermentations there were three molecules of alcohol to one of acetic acid.

Of particular interest is the fact that the organism has no fermentative action on dulcite, the isomer of mannite, which thus furnishes a very striking instance of the selective power of micro-organisms between the most closely allied isomeric bodies. The authors were also unable to cause the organism to ferment solutions of either erythrite, ethylene glycol, calcium, lactate, tartrate, citrate, or glycollate.

In view of the characteristic products—ethyl, alcohol, and acetic acid—of the fermentations, the authors propose for the organism the name of *Bacillus ethacsticus*.

MAGNESIUM AS A REAGENT.

By H. N. WARREN, Research Analyst.

Magnesium, both on account of its purity, and, at the same time, the speed with which it facilitates reduction, either in the moist or dry way, causes it to rank high, if not the first, among reducing agents. Thus, for instance, on account of its purity from arsenic, no agent is, perhaps, better suited for the elimination of pure hydrogen when using Marsh's test for that substance. Secondly, its absence from iron renders it one of the safest reagents for the reduction of ferric salts previous to titration. The speed of reduction, at the same time, being about three times that of zinc, and giving practically no reaction with potassic ferricyanide, the desired absence of both phosphorus and sulphur may also be relied upon. The ease with which it precipitates, from solutions, for instance, zinc, distinguishes it practically from all other metals, separating the same so perfectly that, if to a solution of zinc acetate containing also metals of the fourth group some pieces of magnesium be introduced, and the solution brought to a state of ebullition, the whole of the zinc is thus separated, so as to cause, after the introduction of the necessary reagents to retain in solution the magnesium salts, no precipitate on the addition of ammonium sulphide.

Several samples of zinc ashes containing, as impurities, calcium, magnesium, and other carbonates were quickly assayed by this method, and the zinc estimated in the metallic form.

Its general behaviour with iron salts is somewhat more complex, but, strange to say, from a solution containing a chromic salt, the iron may, with a slight experience, be entirely separated. Take, for example, a sample of chromeisen, to the acid solution of which has been added a sufficiency of sodium carbonate to replace the combined acid. To the precipitated carbonate is added acetic acid in slight excess; if, now, to the acetic acid solution thus formed about 1 grm. of magnesium is introduced, a somewhat violent reaction takes place, the ferric salt becoming almost instantly reduced, and the reaction thus terminating. On the application of heat to the solution the liquid now changes from the deep green characteristic of chromium chloride to a slight pink, thence to a red, violet, and gradually to a pure green, thus assuming its original tint, during which time the iron contained in solution has been precipitated upon the magnesium in a

* Read before the British Association, Section B Newcastle Meeting.

somewhat coherent form, not unfrequently contaminated with oxide of the same. This is to be withdrawn from the solution containing the chromium, boiled with a few drops of HNO_3, and tested for the presence of iron by means of potassium sulphocyanide. As a reagent in the dry way magnesium reduces all metals with the exception of the alkalies and alkaline earths, and may possibly aid in the decomposition of the latter, provided a suitable combination of the same could be obtained.

As an exception to reduction in this line may be mentioned the powerful manner in which it attacts molybdic anhydride, when fused with the same, the combination being so intense as to be accompanied with loud detonations.

Even the refractory substances, silica and boric anhydride, may be also reduced when intensely heated in closed vessels with the same.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 178).

Save for trifling irregularities due to errors of observation, the numbers found agree with the values given above; they are in general rather larger. The precipitates have all essentially an equal and a normal weight. The formation of ammonium phosphomolybdate is completely prevented by $1900-26=1874$ mols. of free NO_3H, but the dissociated compound is separated by an equivalent quantity of nitric acid in excess.

In a solution of a phosphate which contains an excess of nitric acid there must exist, besides the quantity of MoO_3 required for forming phosphododekamolybdic acid, a mol. MoO_3 to every $\frac{1874}{12}=156$ mols. of free nitric acid in excess, in order that the separation of the phosphoric acid may be complete.

5. *Influence of the Proportion of Foreign Salts in the Solution upon the Formation and Separation of the Ammonium Phosphomolybdate.*

As an excess of phosphate or molybdate in a neutral saline mixture involves an increased consumption of acid in the precipitation of the ammonium phosphomolybdate, the presence of other salts of the polybasic acids has a similar action, whilst indifferent salts of monobasic acids, such as the chlorides and bromides, have no perceptible influence upon the course of the reaction. The author therefore confines himself to studying the phenomena in the case of ammonium sulphate and of borax.

On precipitating a neutral solution of ammonium nitrate containing the components of phosphododekamolybdic acid with standard sulphuric acid there were required likewise 23 mols. for the separation of the ammonium phosphomolybdate just as is the case with monobasic nitric acid, though sulphuric acid is bibasic; the conclusion of the reaction was not distinct.

The formation of ammonium phosphomolybdate was attended with the formation of 23 mols. of ammonium hydrosulphate. If the solution already contained sulphate (the proportion of phosphate and molybdate being equal) the consumption of sulphuric acid was still greater, and the greater the richer the solution in sulphate.

Though the distinct determination of the point at which the formation of phosphomolybdate was completed was very difficult on account of the extreme retardation of the separation from solutions containing sulphate, even if nitric acid was added, the following regularities were perceptible:—

The precipitation of the ammonium phosphomolybdate could not be regarded as completed until the typical 23 mols. of hydrosulphate were formed, and when about the tenth part of the extraneous sulphate had been converted into hydrosulphate. It was a matter of indifference whether nitric or sulphuric acid was used for precipitation, and whether ammonium nitrate was present or not.

For precipitating the ammonium phosphomolybdate from 0·010 grm. phosphoric acid and 0·243 grm. molybdic acid from a neutral solution containing—

1	5 grms.	$SO_4(NH_4)_2$	$=269$ mols.
2	5	,,	$=269$,,
3	10	,,	$=538$,,
4	10	,,	$=538$,,

there were required—

1	0·65 grm.	$NO_3H = 73$ mols.
2	0·48 ,,	$SO_4H_2 = 35$,,
3	0·88 ,,	$NO_3H = 99$,,
4	0·68 ,,	$SO_4H_2 = 50$,,

Nos. 3 and 4 contained also NO_3NH_4.

These latter quantities of acid would have produced along with one mol. of $12MoO_3.PO_4(NH_4)_3$ and 12 mols. H_2O:—

	NO_3NH_4.	$SO_4H(NH_4)=n$.	$SO_4(NH_4)_2=m$.	$n-23:m$
1	73	50	219 mols.	1:8
2	—	47	257 ,,	1:10·7
3	99	76	462 ,,	1: 8·7
4	—	77	511 ,,	1:9·5
			In mean	1: 9·2

The number of the mols. of hydrosulphate formed ($=n$), minus 23, is to the unchanged neutral sulphate (m) in the mean as 1 : 9·2. Therefore, as already said in this reaction, 23 mols. of ammonium sulphate and of the rest, on the average the tenth part, had been transformed into hydrosulphate.

In solutions containing very large quantities of sulphate the ammonium phosphomolybdate could not be completely eliminated even when the acidulation of the liquid is conducted very cautiously, and the heating is continued very long. Here, however, the effects of heterostasis and of dissociation are accumulated.*

The relations are simpler with the borates. The separation of phosphomolybdate from solutions containing borates is completed when all the boric acid has been liberated by the nitric acid. This is proved by the following experiment.

A neutral solution containing 0·010 grm. P_2O_5 and 0·243 grm. MoO_3 along with ammonium nitric acid was further mixed with five grms. prismatic borax (*i.e.*, about 93 mols. $B_4O_7Na_210H_2O$ in reference to the mol. of phosphoric acid to be precipitated). In order to re-neutralise the liquid which had been rendered alkaline by the addition of borax, there were required (point not easily distinguished) about 1·50 grms. $NO_3H=170$ mols., and for precipitating the deposit altogether 1·90 grms. $NO_3H=214$ mols. If this number is reduced by the number of the mols. (23) required for converting

$$12MoO_4(NH_4)_2+PO_4H(NH_4)_2$$

into ammonium phosphomolybdate, there then remains

* The term "isostatic" can be applied to that form of combination of a body which involves the simultaneous existence of another body in such a manner that a change of the one involves a change of the other. In this sense the following compounds are isostatic with triammonium phosphododekamolybdic and with each other:—Ammonium hydrosulphate, ammonium hydrophosphate, monammonium-hexamolybdate, and boric acid. Isostasis exists also between triammonium heptamolybdate and triammonium-diphosphopentamolybdate. As heterostatic systems may be mentioned borax and nitric acid, which cannot coexist.

for the conversion of the borax into a condition isostatic with phosphomolybdate 191 mols.

A smaller quantity, 186 mols. NO_3H, is sufficient to liberate all the boric acid in the 93 mols. of borax.

6. Action of Salts, of Water, and Acids upon Preformed Ammonium Phosphomolybdate.

The action of the above-named compounds is very different according to the chemical nature of the bodies, and can be divided into the following three main groups.

1. Ammonium phosphomolybdate is not attacked either in cold or heat by ammonium chloride and nitrate unless the solution is too dilute and slightly acid.

In a perfectly neutral state the above salts do not dissolve any demonstrable quantities in the cold but they eliminate the two loosely combined equivalents of acid, so that the precipitate, after washing with the neutral saline solution, is saturated by 23 mols. of alkali like the phosphomolybdate dried at 150°. Probably in the combination the two mols. of acids which have been eliminated are replaced by as many mols. of neutral salt.

On prolonged heating with a perfectly neutral solution of ammonium nitrate or chloride a trace of the ammonium phosphomolybdate passes into solution and is again separated out by a trace of nitric acid. Perhaps this slight decomposition of the salt depends upon a partially retrograde reaction which tends towards the production of two mols. of nitric or hydrochloric acid, which then combines with the unchanged phosphomolybdate.

2. The ammonium phosphomolybdate is dissolved without the decomposition of the phosphomolybdic acid.

a. On account of a deficiency of ammonium salt in the solution, also by very dilute solutions of ammonium salt (less than 0·4—0·3 grm. NO_3NH_5 in 100 c.c.) on heating and by dilute acids, especially on prolonged heating. The solution in the two first cases are mostly turbid and milky, and can scarcely be clarified, and are yellowish, and on mixture with ammonium nitrate they re-deposit the phosphomolybdic acid which has been in solution.

b. In consequence of a transformation to soluble phosphomolybdate, on contact with sodium chloride or nitrate ammonium phosphomolybdate dissolves quickly, if heated, to a yellow solution of sodium phosphomolybdate, which forms a precipitate with ammonium salt. Chlorides and nitrates whose bases can form soluble phosphomolybdate act in a similar manner.

Potassium chloride and nitrate have only a slight action on account of the sparing solubility of potassium phosphomolybdate.

3. Ammonium phosphomolybdate dissolves with a more or less complete decomposition of the phosphomolybdic acid.

a. In consequence of an action which is tantamount to a partial saturation by alkali.

By heating with water considerable quantities of ammonium phosphomolybdate can be dissolved in a short time. The strongly acid solution, opalescent and more or less deeply yellow, according to the time of the action, is coloured a bright yellow on the addition of a few drops of nitric acid, and gives a strong precipitate with ammonium nitrate. Such a precipitate is produced by ammonium salt, even in a solution which has not been previously mixed with nitric acid. The filtrate, on the addition of a few drops of nitric acid, deposits a larger or smaller quantity of precipitate. The first precipitate, in proportion to the second, is the more abundant the longer the action of the water has lasted.

The salts of polybasic inorganic acids in degrees of saturation not isostatic with phosphomolybdate dissolve the yellow precipitate sparingly in the cold, but readily on heating, forming—even if the salt was neutral—colourless, strongly acid solutions, which, if mixed with nitric acid, re-constitute the yellow compound. Thus behave the neutral sulphates, phosphates, hydrophosphates, molybdates, &c.

The action of the salts of organic acids is quite analogous to that of free alkali. But, whilst the ammonium phosphomolybdate is completely separated out by nitric acid from the solutions of the salts of monobasic acids, provided there is a sufficiency of ammoniacal salt, and all the organic acid is set at liberty, the presence of polybasic acids, such as the oxalic and tartaric, prevents entirely the re-union of the elements of the phosphomolybdic acids, which appears from the fact that the colourless solution, on acidulation with nitric acid, neither gives a precipitate nor takes a yellow colour.

(To be continued).

THE MOLECULAR WEIGHTS OF CERTAIN SUBSTANCES AS INDICATED BY THE BOILING-POINTS OF THEIR SOLUTIONS.

By H. W. WILEY.

The apparatus with which the experiments to be described below were made was devised in August of this year, and the experiments were commenced about September 1. It was not my intention to publish the results of this work until they had been greatly extended, but the notice of the observations of Ernest Beckman of his employment of the same method induces me to submit the data already obtained for publication.

I have no desire whatever to question Mr. Beckman's priority in the use of the method, but it may be of interest to know that it was independently adopted by me, and all the data submitted below obtained before a notice of his work reached me in the *Chemisches Central-Blatt*, No. 7, 1889, this day received.

The apparatus employed consisted of an oval-round bottom flask of about 200 c.c. capacity, the neck of which was supplied with a side tube for the purpose of connecting it with an appropriate condenser. By this means the volume of the liquid employed was kept constant. The thermometer employed was accurately graduated to tenths, the distance between each tenth of a degree being so great that with the aid of the cathetometer used in reading it we could easily distinguish the 0·02 of a degree. The bulb of the thermometer was made to occupy the central portion of the liquid, the volume of which in all cases was 150 c.c. To protect the bulb of the thermometer against the influence of the steam bubbles it was covered with a double coating of fine copper foil. This method of coating the bulb of the thermometer of course precluded its use with substances easily reduced, such as silver and mercury salts.

Sodium chloride was the substance chosen to determine the factor for use. Carefully repeated determinations with this substance gave the following data:—

Substance taken	Sodium chloride.
Volume of water	150 c.c.
Weight of substance taken	4·5 grms.
Weight of substance taken to 100 c.c. of water	3·0 grms.
Boiling-point of water	99·47°
Boiling-point of sodium chloride in solution	99·93°
Total rise of temperature	0·46°
Rise of temperature for 1 grm. per 100 of substance..	0·1533°
Molecular weight of sodium chloride..	58·5

Factor = 0·1533 × 58·5 = 8·968.

Using this factor as a constant the accompanying determinations have been made (see Table, next page).

In addition to the numbers given above a large number of determinations have been made with substances containing water of crystallisation. In those cases the calculated molecular weight does not correspond either

Substance taken.	Volume water.	Wt. substance taken in grms.	Wt. substance taken in grms. to 100 c.c. water.	Temperature of boiling water.	Boiling temperature of substance in solution, °C.	Total rise of temperature, °C.	Calculated molecular weight.	Theoretical molecular weight.
KCl	150	6·0	4·0	99·50	99·85	0·35	76·91	74·5
KBr	150	6·0	4·0	99·50	99·79	0·29	123·7	119·0
KI	150	9·0	6·0	99·50	99·83	0·33	163·1	166·0
KNO_3	150	6·0	4·0	99·50	99 83	0·33	108·7	101·0
$K_2Cr_2O_7$	150	18·0	12·0	99·50	99·88	0·38	283·2	295·0
$NaNO_3$	150	6·0	4·0	99·44	99·86	0·42	85·4	85·0
Sucrose	150	20·0	13·33	99·50	99·70	0·20	643·2	342·0
Oxalic acid ..	150	6·0	4·0	99·50	99·70	0·20	179·4	90·0

with the theoretical molecular weight, including the water of crystallisation, nor with the molecular weight of the anhydrous salt. These results seem to indicate that substances containing water of crystallisation exist in solution in a modified form, and the influence of this modification on the boiling-point of the solution can only be determined by largely extended observations.

It is curious to note further that in the two organic substances examined the observed molecular weight obtained, using the same factor obtained by observations on the sodium chloride, is just about double the ordinary accepted molecular weight.

Since the factor for boiling solutions is so much less than that for the freezing mixtures, the determination of the molecular weight by the above method requires a solution considerably stronger than that used in Raoult's freezing method. The advantage, however, of having a mercurial column sensibly constant for long intervals of time renders it possible to make the observations with great accuracy.

To allow for the slight changes which take place in the boiling-point of water under the conditions mentioned, I propose, hereafter, to use two pieces of apparatus, one of which shall contain water to be kept constantly in use, the observation of the boiling-point of water and of the substance under examination being made at the same time. It is hardly necessary to mention that in such a case the thermometers employed would be carefully compared and the readings corrected accordingly. It is further necessary that the source of heat be sensibly constant, and we secure this by using a lamp with a certain sized flame which remains unchanged throughout the whole series of observations.

For assistance in the analytical data obtained I am indebted to Mr. W. H. Krug.

Sept. 14, 1889.

ON THE

COLOURS PRODUCED DURING THE TEMPERING OF STEEL.*

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It has long been observed, and every steel worker knows, that when bright steel is heated in the air to certain definite temperatures, a series of colours can be obtained, beginning with a light straw, and passing through a succession of brown and purple shades to a deep blue. These colours have attracted the attention of many observers, and suggest questions of interest as to the causes and circumstances of their production, and the physical and other problems therewith connected. In addition, however, to any other cause of interest these colours possess, they have been studied on account of their real and supposed importance in the arts. Everyone must be familiar with the different shades of colour which are given to steel pens, varying from a very light straw to a deep purple or blue. These various shades are commonly produced by heating the clean bright pens, in their otherwise finished condition, to a suitable temperature in a revolving cylinder. When the desired colour has been obtained the pens are immediately cooled by being turned quickly out on to a sieve or other cooling place, so that the colour produced may not change by further heating. The colours of the pens met with in commerce are, however, not quite the same as those produced as above described, since the tints are slightly altered by the lacquer which is used to prevent rusting. Another well-known application of these colours is in the ordinary method of tempering steel, which is a very important, though, in many cases, an extremely delicate operation. After the steel has been hardened, say, in the form of a plain drill or chisel or other simple tool, the workman commonly cleans a portion of the surface of the steel, and then once more cautiously heats it until a certain desired colour is obtained on the bright surface; the tool is then usually immediately cooled in water. It will be seen, therefore, that the formation of a particular colour is assumed to correspond more or less nearly with a certain combination of hardness and tenacity which is required in the tool, and when it is remembered that usually the value of the tool is dependent to a very considerable extent on the temper which is imparted to it, and that the workman judges of this temper by the colour of the surface, it will be seen that the study of the properties of these colours is of great importance to thousands of workshops in this country. Further, the whole range of temperature used in tempering steel generally extends only from about 220° to 320° C., or thereabouts, that is, only about 100° C. (though we have good reason to believe that this range is capable of extension); it will be seen, therefore, that it must involve very considerable experience to successfully temper a piece of steel when the operator is obliged to work in the manner above described.

Thus, within the range of only one hundred degrees Centigrade, we have compressed the points which are necessary for the proper treatment of a knife-edge and a cold chisel, a razor and a spring, a steel engraver's tool and a saw, a lancet and a hatchet, tools as opposite as possible in properties and uses, and each and all of which would be entirely unfitted for their purpose if treated improperly during tempering. It is no exaggeration to say that a difference of only ten degrees Centigrade would often exert a considerable influence on the usefulness of a tool, and yet in most cases the workman can only judge of the temperature employed by the colour he observes. How far this is a trustworthy guide we shall consider anon, but it is of interest to notice that almost exactly a century ago, on June 9, 1789, a patent (1687) was granted to David Hartley for the use of a "pyrometer or thermometer, or other precise or regulated mode of measuring heat in tempering articles made of steel, instead of the mode hitherto accustomed of tempering them by colour," and Hartley stated that usually the tempering heats "lie between the points of four hundred and six hundred degrees upon Fahrenheit's scale of heat." For delicate work the thermometer has been more or less in use ever since Hartley's time.

Several writers (including Aikins, Jeans, and others) have attributed the use of a fusible metal bath, and the

* A Paper read before the Birmingham Philosophical Society, June 13, 1889.

determination of colour temperatures, as now generally received, to Hartley. Certainly, fusible metal and other baths were used early in the present century (see Aikins' "Chem. Dict.," 1807, vol. i., p. 604), but I have not been able to establish any connection between these and Hartley, whose patent above quoted gives most general directions for applying heat, evidently without later refinements, and gives no more details of temperature than above quoted. The best and most complete colour-tempering scale with which I am acquainted was published in the form of a coloured diagram with the "Report of the United States Chief of Ordnance," 1885, p. 204.

Most writers who touch on this subject treat it in a stereotyped manner, stating that when bright steel is heated to a certain temperature, such and such a colour is produced, and this is suitable for lancets, chisels, springs, or other articles, as the case may be. It is, therefore, tacitly assumed, though not perhaps actually stated, that a particular colour corresponds to a certain temper, and is invariably produced at a particular temperature. In fact, the three things—colour, temper, and temperature—might, so far as the text-books are concerned, be closely and for ever united.

The cause of the production of these colours is now universally, I believe, acknowledged to be the formation of thin films of oxide on the surface of the metal when it is heated in presence of air. Even this question was at one time in dispute, such men as Davy ("Chemical Phil.," p. 390) and Thomson ("Chemistry," vol. i., p. 224) taking the opposite view. But Davy afterwards showed ("Thomson's Annals," 1813, vol. i., p. 131) that steel might be heated in a neutral gas, such as hydrogen or nitrogen, without being coloured on its surface, and that steel remained colourless when heated under the surface of oil or of mercury.* I have frequently heated bright strips of polished steel for hours under the surface of mercury or oil without discolouration, while they would have been instantly coloured at the temperature used if heated in contact with air. I think, further, that there can be little doubt that the oxide so produced is practically transparent, first, because the sequence of colours is what would be expected in films of a transparent substance when the thickness of the films gradually increases; also because of observations on the reflected light, the colour of which varies somewhat at different angles; but chiefly because it is found that on increasing the temperature a little above the point necessary to produce a dark blue, the colour gradually disappears (though doubtless oxidation proceeds more rapidly), and the surface, though covered with more oxide, becomes almost colourless again.

When it is granted that the colours we are considering are the result of oxidation, it would at once appear probable that the nature of the surface to be heated, its freedom from dirt and grease, and the length of time during which it is heated, would all exert a considerable influence on the shade produced. It would also appear probable that the amount of carbon present in the metal, and the condition in which the carbon existed, would have comparatively little influence. Hitherto my experiments have been chiefly directed to the study of these simple and, as they appear, almost self-evident conclusions.

Heating has usually been performed in a large air oven, inside of which, about two inches from the bottom, was an iron tray, supported on fire bricks, and filled with sand to the depth of about an inch, a small space being left all round the tray so as to prevent contact with the sides of the oven. Resting on the surface of the sand, but not touching the edges of the tray, was a plate of copper, on which were placed the strips of steel it was desired to heat. The object of this arrangement was to prevent irregular heating from below, and to give as much uniformity as possible. Passing through the centre of the copper plate, and partly covered by the sand, was the thermometer used; and, as even with these precautions it was not found possible to get perfect uniformity, a considerable number of strips was operated upon at one time, and about four removed, from different parts of the plate, when an observation was made. I am indebted to Messrs. Perry and Company, Limited (late Sir Josiah Mason) for specimens of bright crucible pen steel, both in the soft and in the hardened condition, while Mr. G. H. Strick, of Brynamman, kindly supplied me with samples of bright wrought-iron.

It is, of course, necessary that for such experiments the steel to be used should be clean and bright. A rough surface does not give nearly the same brilliancy of colour as is noticed when the metal is carefully polished, though the shade is pretty nearly the same in both cases. The presence of dirt usually causes irregular colouring, producing bands or spots of colour different to the rest of the surface. Naturally, too, some kinds of dirt appear to assist oxidation, though the shade is less brilliant, while other kinds of dirt exert a protective influence. The brightest shades are produced with perfectly clean and polished surfaces, and few people are aware of the gorgeousness of the shades of purple and blue which can be produced on a large surface with proper conditions.

In connection with the supposed relationship between colour and temper, I have taken strips of bright steel, hardened and unhardened, and also bright wrought-iron, and heated them as above described at various temperatures, for definite periods, and find that practically each of these three varieties of iron gives the same colours in the same time. The only difference I have been able to perceive is that the hardened steel gives the brightest colour, and the wrought iron the least brilliant. This difference in brilliancy is, no doubt, due to the fact that the surface was more perfect in the hardened steel specimens, which had been carefully cleaned by rotation with sand in barrels for a lengthened period. The fact that in each of the three cases the shade produced under similar circumstances is identical shows at once that the colour on a steel tool is no indication whatever as to the content of carbon or the temper of the steel.

As bearing on this aspect of the question it may be mentioned that Bousfield patented (1866, No. 2810) a method of blueing the surface of sheet iron. After the sheets had been properly cleansed they were heated in an air-tight flask for a good many hours at 700° F., care being taken that no two sheets were in contact with each other. Probably a lower temperature and a shorter time, with free access of air, would produce a similar result. I notice, too, that in some cases cast-iron is coloured in a similar manner, and this fact confirms the above conclusions.*

From the very beginning of my experiments I have been struck with the fact that *time* has a most important influence in developing these colours. From a study of ordinary text-books one might readily conclude that to produce a light straw colour about 221° C. is necessary, while about 320° C. is required to produce a blue colour. Such a conclusion would, however, be quite erroneous, for it is easy, by heating the specimens for a comparatively lengthened period, to produce a *blue* colour at a temperature *below* that which is usually regarded as necessary to give a *straw colour*, or over 100° below that which is generally accepted as producing a blue. In the same way a straw colour can be produced, in a few minutes, fully 50° below 221° C., which is the generally accepted temperature. It will be found, however, that, as we pass from shade to shade up the series, each colour requires a longer interval for its production at a given temperature than the one which preceded it. Thus, at a

* Professor Roberts-Austen has also shown that steel is not coloured when heated in vacuo (Inst. M. E., 1881, p. 710).

* Dr. Percy has given details of the methods used to obtain the bright grey-black coating on Russian sheet-iron. "Manufacture of Russian Sheet-iron, 1871." The colour in this instance is partly due to carbonaceous matter.

given temperature, we may pass from very light straw to straw, a well-marked change, in a few minutes, while at the same temperature it may require almost as many hours to pass from purple to blue. Further, in starting with low temperatures, the intervals of time between the various shades are greater, and becomes very considerable indeed for the deeper shades. For example, a purple can be produced at 250° in a few minutes which would require an hour at 220°, or about twelve hours at 170°, though the ultimate result would be the same in each case.

On the other hand, it can be shown that, with a deficiency of oxygen, iron or steel may be heated far above the temperatures previously mentioned without producing the usual succession of colours. Thus, in annealing sheet-iron in the manufacture of tin plates, a number of sheets are heated to redness for some hours in an iron box, from which the air is excluded as far as possible. On removing the sheets when cold they are found to be straw-coloured or brown in the centre over perhaps two-thirds of their area. Surrounding this centre portion, passing outwards in order, are found purple, blue, light blue, blue green, and nearly colourless, depending on the amount of oxidation, though the sheets themselves have been exposed for a considerable time to a red heat. Bousfield's patent, above mentioned, is another example of the same kind.

Details of a few of my own experiments, undertaken to try and determine the interval between definite shades, may serve to illustrate these facts. Thus:—

Total Time of Heating at 221°—227° C.	Interval between Samples.	Colour.
5 mins.		Dark straw.
12 ,,	7 mins.	Brown.
21 ,,	9 ,,	Brown, with purple.
32 ,,	11 ,,	Nearly all purple.
45 ,,	13 ,,	Purple, with some blue spots.
60 ,,	15 ,,	Very similar.
77 ,,	17 ,,	Nearly all blue.
95 ,,	19 ,,	Very similar.
117 ,,	21 ,,	Deep blue.
140 ,,	23 ,,	Blue, with a slight tinge of green.

It will be seen, on examination of the specimens shown that several of the above colours are "bastards," *i.e.*, transition-colours, and that although the last interval (twenty-three minutes) is more than four times as long as the first (five minutes), still the early intervals are too long, and the later ones too short. Another experiment gave:—

Total Time of Heating at 220°—227° C.	Interval between Samples.	Colour.
1 min.		Very light straw.
4 ,,	3 mins.	Light straw.
9 ,,	5 ,,	Straw.
16 ,,	7 ,,	Brown.
25 ,,	9 ,,	Brown, with purple.
36 ,,	11 ,,	Brown and purple, about equal.
49 ,,	13 ,,	Purple, with some brown.
64 ,,	15 ,,	Purple, with blue.
81 ,,	17 ,,	Nearly all blue.
100 ,,	19 ,,	Blue.

In this experiment, though the time of heating varied the squares of the numbers from one to ten, still the intervals were too short in the later samples, and transition colours were obtained. The earlier samples, also, were not so definite as might be desired, though it would be difficult to express the slight variations in words. The following was a more successful experiment:—

Total Time of Heating at 220°—227° C.	Interval between Samples.	Colour.
2 mins.		Very light straw.
4 ,,	2 mins.	Straw.
8 ,,	4 ,,	Dark straw.
16 ,,	8 ,,	Brown.
32 ,,	16 ,,	Brown, with purple.
64 ,,	32 ,,	Purple.
128 ,,	64 ,,	Dark blue.
256 ,,	128 ,,	Greenish blue.

The three series of steel test pieces, as above, are exhibited in the room, and it is evident to all that the last of the three experiments gave far the best results, as judged by the distinctness of the shades produced. Hence at the temperature used (220°—227° C., corresponding closely with 221°, commonly accepted as giving a straw colour), the time required to pass from one distinct shade or colour to the next increases approximately in geometrical progression. Dr. Poynting has suggested that at the temperatures used in my experiments the film of oxide first formed may act as a protection to the surface of the metal, and that the rate at which the thickness of the film increases may be represented by a logarithmic curve. I do not venture to suggest that a similar rule would hold good for all temperatures, of that I have no evidence; but this is certain, that at low temperatures, such as, say, 150°, the various colours can be produced, but it requires very prolonged heating in order to obtain the blue shades. On the other hand, the lighter colours can be produced at a high temperature, but require very little time for their development. I have not attempted to determine the lowest temperature at which these colours can be produced, and should imagine it would be difficult to do so accurately. I have, however, succeeded very well at 150°—160° C., and do not doubt that with sufficient time a still lower temperature will suffice.

Though the foregoing observations prove that the colour developed is dependent as much upon time as upon temperature, and that the colour is independent alike of the amount and the condition of the carbon present, so long as the surfaces and other conditions are alike; still these observations merely suggest another and more important question, namely, how far the temper of the steel may be affected, and its properties changed, by continued heating at a temperature below that which is generally employed for tempering. Hitherto I have not been able to obtain quantitative results in this connection, owing to the fact that steel strips, even when carefully hardened, not only differ in the various pieces, though cut off the same sheet and treated in the same manner, but even the same strip will very commonly differ in hardness on the two sides, and not unfrequently, even in a strip of only some three inches in length, one side of the strip will be different at each end, while the middle will not agree with either. Hence some more satisfactory method of experiment is required; but in the meantime I have satisfied myself that hardened steel strips, if heated for some hours at 220° C., are distinctly softer than similar strips which have been heated for a shorter time; and that, though a few minutes at 220° produces a distinct effect, the interval has to be considerably increased from time to time in order to produce further and further appreciable softening of the steel.

I am informed that the experience of steel pen manufacturers lends support to the above opinions, and I may venture, in conclusion, to refer to other observations in the same direction. Brande ("Chemistry," 1848, vol. i., p. 759) gives the following interesting details in reference to the preparation of knife-edges for a pendulum used by Capt. Kater (*Phil. Transactions*, 1818, p. 38), the details of which preparation were not given in Capt. Kater's original paper. Brande states that the knife edges "were

forged by Mr. Stodart from a piece of fine wootz; they were carefully hardened and tempered in the bath at 430° F.; on trial they were found too soft. They were a second time hardened, and then heated to 212°. The intention was to increase the heat from that point, trying the temper at the advance of about every 10°. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered." "It is highly probable," Brande continues, "that steel for many uses may be sufficiently tempered in a range so extensive as from 212° to 430° (100° to 221° C.). But it is *not the temperature only, but also the time during which the steel is exposed to it*, which influences its hardness or temper." The italics in the above quotation are mine.

As confirming the view that steel may be tempered at at a lower temperature than is usually supposed, there are also the experiments of Professor Langley (Inst. M. E., 1882, p. 148), who showed that the density of steel was distinctly reduced (*i.e.*, the steel was hardened) by cooling rapidly from the boiling point of an alkaline solution used for removing the scale from the specimens examined. So far as my observations have gone I believe—

1. In the words of Brande:—"It is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper."

2. High carbon steels are more sensitive to the effects of comparatively low temperatures than are steels containing less carbon.

3. The colours observed in tempering steel can be produced by suitably varying the conditions, at temperatures far either above or below those usually accepted as necessary to produce a particular shade; the colours can be produced alike with hardened or with unhardened steel; and with wrought-iron or cast-iron as well as with steel. They are, therefore, independent of the amount or condition of the carbon present in the steel.—*Proceedings of the Birmingham Philosophical Society*, Vol. vi., Part 2.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 184).

PROBLEM XI. *To Determine whether Oxides such as Water and Chalk Gas may be Deprived of Oxygen by means of Metals.*—It being found that hydrogen and carbon withdraw the oxygen from some but not from all metals, it follows that some metals have a stronger, others a weaker, hold upon or "affinity" to oxygen than has either oxygen or carbon; the question arises whether any and which metals have so much greater an affinity to oxygen that they will withdraw it from hydrogen and carbon. Copper and iron have been found to part with oxygen, but zinc and magnesium did not; so these four metals may be studied comparatively. Steam is passed through a red-hot copper tube full of copper tacks: no change is observed. The experiment is repeated with an iron tube charged with bright iron nails: a gas is obtained which is soon recognised to be hydrogen, and on emptying out the nails they are found to be coated with black scale. Zinc and then magnesium are tried, and, like iron, are found to liberate hydrogen. Chalk gas is next passed over red-hot copper, and is found to remain unchanged, but on passing it over red-hot iron or zinc a gas is obtained which burns with a clear blue smokeless flame: this gas is not absorbed by milk of lime, but on combustion yields chalk gas, so it evidently contains carbon, and is a new combustible gas. Like hydrogen it is found to afford an explosive mixture with oxygen. Finally, magnesium is heated in chalk gas: it is observed to burn, and the magnesium to become converted into a blackish substance unlike the white oxide formed on burning it in air. But it is to be expected that this oxide is produced, and to remove it, as it is known from previous experiments to be soluble in muriatic acid, this acid is added: a black residue is obtained. What is this? Is it not probable that it is carbon? If so, it will burn in oxygen yielding chalk gas. So the experiment is made. These experiments in which hydrogen is obtained from water and carbon from chalk gas afford the most complete "analytic" proof of the correctness of the conclusions previously arrived at regarding water and chalk gas, and which were based on "synthetic" evidence; taken together, they illustrate very clearly the two methods by which chemists determine composition.

As hydrogen and carbon form oxides from which oxygen may be removed by means of some metals, but not by all, the question arises, which has the greater hold upon or affinity to oxygen—carbon or hydrogen? As it is the easiest experiment to perform, steam is passed over red-hot charcoal: a combustible gas is obtained which yields water and chalk gas when burnt, so evidently the hydrogen is deprived of its oxygen, and this latter combines with the carbon, forming the combustible oxide of carbon. Will not carbon partly deprive chalk gas of its oxygen? The experiment is made and it is found that it will. These results afford an opportunity of calling attention to and explaining the changes which go on in ordinary fires and in a furnace.

PROBLEM XII. *To Determine the Composition of Salt Gas, and the Manner in which it Acts on Metals and Oxides.*—It has previously been demonstrated that spirits of salt or muriatic acid is prepared by acting on salt with oil of vitriol and passing the gas which is given off into water; the solution has been found capable of dissolving various metals and oxides, chalk, lime, &c., and as water alone does not dissolve these substances the effect is apparently attributable to the dissolved gas, so it becomes of interest to learn more of this gas in order that its action may be understood. It is first prepared; its extreme solubility in water is observed, and also the fact that as it dissolves much heat is given out; and it is noted that although colourless and transparent it fumes in the air. How is its composition to be determined? Is there any clue which can be followed up? Reference is made to the previous observations, and it is noted that its solution dissolves various metals with evolution of hydrogen; water alone has no such effect. Is this hydrogen derived from the water or from the dissolved gas? The gas alone is passed over heated iron-turnings, and the escaping gas is collected over water; it proves to be hydrogen, so evidently salt gas is a compound of hydrogen with something else. How is this something else to be separated from the hydrogen? Do not previous experiments suggest a method? Yes, they have proved that hydrogen has a marked affinity to oxygen, and now it is recollected that on treating muriatic acid with red lead—a substance rich in oxygen—a greenish yellow gas is obtained. The experiment is repeated on a larger scale and the gas is examined. If it is contained together with hydrogen in salt gas, perhaps salt gas will be obtained on applying a flame to a mixture of the two gases just as water is from a mixture of oxygen and hydrogen: the mixture is made and fired, and the result leaves little doubt that salt ga does consist of hydrogen in combination with the greenish yellow gas—chlorine. Whence is this chlorine derived—from the salt or the sulphuric acid?

The notes are again consulted, and it is seen that a solution of silver in nitric acid gave a characteristic precipitate with muriatic acid but not with sulphuric, so salt solution is added to the silver solution, and a precisely

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

similar precipitate is obtained, leaving little doubt that the chlorine is derived from the salt. It is now easily realised that the iron and zinc displace the hydrogen of the dissolved hydrogen chloride. What happens when the oxides are acted on? In addition to the metal they contain oxygen, which is known to combine readily with hydrogen, forming water; is water formed? Lime oxide is therefore heated in hydrogen chloride; a liquid is obtained which behaves exactly as a solution of hydrogen chloride in water. When the action is complete, after driving off all that is volatile, a solid remains very like fused common salt—doubtless zinc chloride, as it is to be supposed that as the hydrogen has taken the place of the zinc the chlorine has taken the place of the oxygen. What, then, is the action of hydrogen chloride on chalk? It evidently not only separates the chalk gas from the lime, but also dissolves this latter. What is formed? Dry (unslaked) lime is therefore heated in a current of hydrogen chloride. It behaves just as zinc oxide, yielding a liquid product—evidently a solution of hydrogen chloride in water, as it dissolves zinc with evolution of hydrogen, and the residue is like that of zinc chloride. The important discovery is thus made that lime also is an oxide—that chalk, in fact, is a compound of two oxides; the resemblance of lime to zinc oxide and magnesium oxide is so striking that the conclusion is almost self-evident that lime is probably a metallic oxide, and it may be here pointed out that this actually is the case. The gradual discovery of the composition of chalk in the manner indicated is an especially valuable illustration of chemical method, and serves to show how chemists are often obliged to pause in their discoveries and to await the discovery of new facts and methods of attack before they are able to attack before they are able to completely solve many of the problems which are submitted to them. The solids obtained on dissolving zinc oxide and lime in muriatic acid and boiling down the solution, when all the water is driven off, are white solids like fused salt, but on exposure they gradually become liquid. In so doing they increase in weight, and evidently behave like sulphuric acid. Probably water is absorbed from the air: no change takes place when they are kept over sulphuric acid or dry lime. In this way two new desiccating agents are incidentally discovered.

Problem XIII. *To Determine the Composition of Washing Soda.*—The study of this substance is of importance as introducing the conception of an alkali. The preparation from salt is first described. On heating the crystals they melt and give off "steam"; the experiment is made in such a way that a quantity of the liquid is obtained sufficient to place beyond doubt that it is water. The water is found to be easily driven off on heating the crystals in the oven, and to constitute a very large proportion of the weight of the crystals. The conception of water of crystallisation is thus gained. On heating the dried substance to full redness in the platinum dish, no loss occurs. The residue dissolves in water, and "soda crystals" may again be obtained from the solution, so that heat does not affect it. Perhaps acids which have been found to act so powerfully in other cases will afford some clue—on trial this is found to be the case: a colourless odourless gas is given off, which extinguishes a burning taper. Is this perhaps nitrogen or chalk gas? The lime water test at once decides that it is the latter. So it is determined that washing soda, like chalk, is a compound of chalk gas—but with what? With an oxide? The dried substance is heated in hydrogen chloride: chalk gas is given off as before, and a liquid which is soon recognised as water saturated with hydrogen chloride. The residue dissolves in water, and separates from the concentrated solution in crystals exactly like salt, and, in fact, is soon recognised to be salt; evidently, therefore, that which is present in salt along with chlorine is present in soda crystals along with oxygen, chalk gas, and water. The preparation of the metal sodium from soda is then explained. Acquaintance being thus made with compounds of chalk gas with two different oxides, the question arises, which oxide has greater affinity to the chalk gas? Will lime drive sodium oxide from soda or *vice versâ*? On adding lime water to soda solution a precipitate of chalk is formed. What does the solution contain? Lime water contains lime in combination with water; is the sodium oxide present in combination with water? Soda is boiled with milk of lime (in an iron saucepan to avoid breakage) until it no longer affects lime water; afterwards the liquid is poured off and boiled down. The product is very unlike soda: it is very caustic, and when exposed to the air becomes liquid. If it is an analogous substance to slaked lime, it should combine with chalk gas and be reconverted into soda; this is found to be the case. Caustic soda is thus discovered. Chalk and lime are known to neutralise acids; both soda and caustic soda are found to do so, and their effect on vegetable colours is found to be the reverse of that of acids. At this stage the origin of the name alkali is explained, and it is pointed out that the oxides which have been studied may be arranged in two groups of alkali-like or *alkylic* and acid-forming or *acidic* oxides, the former being derived from metals, the latter from non-metals. The production of *salts* by the union of an oxide of the one class with the oxide of the other class is then illustrated by reference to earlier experiments.

The point is now reached at which the results thus far obtained may be reconsidered. The student has been led in many cases to make discoveries precisely in the manner in which they were originally made; and it is desirable that at this stage, if not earlier, the history of the discovery of the composition of air and water, &c., should be briefly recited. It is then pointed out that a variety of substances have been analysed and resolved into simpler substances—air into oxygen and nitrogen, water into oxygen and hydrogen, &c.; and that these simpler substances thus far have resisted all attempts to further simplify them, and are hence regarded as elements. A list of the known elements having been given, the diverse properties of the elements may be illustrated from the knowledge gained in the course of the experiments. The fact that when elements combine compounds altogether different in properties from the constituents are formed also meets with manifold illustration. Too little has been ascertained to admit of any general conclusion being arrived at with regard to the proportions in which elements combine, but it clear that they may combine in more than one proportion since two oxides of carbon have been discovered, and in the only cases studied—viz., copper oxide and chalk—the composition has been found not to vary. The existence of various types of compounds has been recognised, and a good deal has been learnt with reference to the nature of chemical change. But, above all, the method of arriving at a knowledge of facts has been illustrated time after time in such a manner as to influence in a most important degree the habit of mind of the careful student. New facts have been discovered by the logical application of previously discovered facts: the logical use of facts, and the habit of using facts have been inculcated. This is all-important. It has become so customary to teach the facts without teaching how they have been discovered that the great majority of chemical students never truly learn the use of facts; they consequently pursue their daily avocations in a perfunctory manner, and only in exceptional cases manifest those qualities which are required of the investigator; their enthusiasm is not awakened, and they have little desire or inclination to add to the stock of facts. It must not for one moment be supposed that the object of teaching chemistry in schools is to make all chemists. Habits of regulated inquisitiveness, such as must gradually be acquired by all who intelligently follow a course such as has been sketched out, are, however, of value in every walk of life; and certainly the desire to understand all that comes under observation should as far as possible be implanted in everyone.

Stage V.—*The Quantitative Stage.*

The *quantitative* composition of many of the substances which have previously been studied qualitatively should now be determined—in some cases by the teacher in face of the pupils, so that every detail may be odserved and all the results recorded; in other cases by the pupils.

The composition of water is first determined by Dumas's method; this may easily be done, and fairly accurate results may be obtained in the course of a couple of hours. The results obtained by Dumas and subsequent workers should then all be cited, and, attention having been drawn to the extent to which such experiments are necessarily subject to error, the evidence which the results afford that hydrogen and oxygen combine in certain *fixed and invariable proportions* to form water is especially insisted upon.

The composition of chalk gas is next determined; this also is easily done, as impure carbon (lampblack) may be burnt and the hydrogen allowed for. Again, attention is directed to the results obtained by skilled workers, and the evidence which they afford that chalk gas never varies in composition.

The composition of copper oxide has already been ascertained; it may be re-determined by reducing the oxide in hydrogen: in fact, in determining the composition of water.

The lead oxides may be reduced in a similar manner, the oxide obtained by igniting white lead as well as red lead and the brown oxide obtained by treating red lead with nitric acid being used. In this way it is ascertained that the brown oxide is the highest oxide; the loss in weight which this oxide suffers when ignited may then be determined.

Tabulating the results thus obtained, after calculating with what amount of the particular element that quantity of oxygen is associated which in water is combined with one part by weight (*unit weight*) of hydrogen, numbers such as the following are obtained:—

Parts.			Parts.		
1	hydrogen	is combined with	8	oxygen	in water
3	carbon	,, ,,	8	,,	chalk gas
31·5	copper	,, ,,	8	,,	copper oxide
103·5	lead	,, ,,	8	,,	lead oxide (litharge)
51·8	,,	,, ,,	8	,,	lead oxide (brown).

These clearly illustrate the fact that elements combine in very different proportions, and the results obtained with the lead oxides afford also an illustration of combination in multiple proportion.

The amounts of silver and lead nitrates formed on dissolving silver and lead in nitric acid are next determined by evaporating the solutions of known weights of the metals in porcelain crucibles on the water-bath, and then drying until the weight is constant; accurate results may be easily obtained, and these two exercises afford most valuable training. The nitrates are subsequently evaporated with muriatic acid and the weights of the products determined. What are these products? Does the metal simply take the place of the hydrogen in hydrogen chloride as zinc does when it dissolves in muriatic acid? If so, the products are silver and lead chlorides, and it may be expected that the same substances will be obtained—that the same increase in weight will be observed, when, say, silver is combined directly with chlorine as when it is dissolved in nitric acid and the solution is precipitated with muriatic acid or salt. Silver is, therefore, heated in chlorine, and is found to increase in weight to the same extent as when it is dissolved in nitric acid, &c.; a given weight of silver precipitated by salt is also found to increase to the same extent as when it is directly combined with chlorine. The composition of silver chloride having thus been ascertained, the amount of chlorine in salt is determined. The composition of salt being ascertained, purified dried washing soda is converted into salt, and also the amount of chalk gas which it contains is determined: from the data, the composition of sodium oxide may be calculated. In like manner the composition of lime may be ascertained by converting chalk into chloride, by igniting it in hydrogen chloride, and then determining the chlorine in the chloride; the same method may be applied to the determination of the composition of the oxides and chlorides of zinc, magnesium, and copper.

Discussing these various results, and comparing the quantities of oxygen and of chlorine which combine with any one of the metals examined, it is seen that in every case about 35·4 parts of chlorine takes the place of eight parts of oxygen. Combination in *reciprocal proportions* is thus illustrated, and by considering the composition of chalk and washing soda it may be shown that this applies equally to compounds of two and to compounds of three elements. As 35·4 parts of chlorine is found in every case to correspond to eight parts of oxygen, it is to be expected that hydrogen chloride contains one part of hydrogen in combination with 35·4 parts of chlorine; a solution containing a known weight of hydrogen chloride is, therefore, prepared by passing the gas into a tared flask containing water, and the chlorine is then determined.

It being thus clearly established what are *equivalent* weights of elements, the conception of equivalents may be further developed by exercises in acidimetry carried out by the pupils themselves. The proportions in which washing soda and hydrogen chloride interact may be determined by mixing solutions of known strength until neutralisation is effected; if the solution be evaporated and the chloride weighed, the results may be used in calculating the composition of hydrogen chloride; they serve, in fact, as a check on the conclusions previously arrived at as to the composition of washing soda and hydrogen chloride. Solutions of sulphuric and nitric acid may be similarly neutralised, and, the amounts of sulphate and nitrate formed having been ascertained, the equivalents of the acids may be calculated on the assumption that the action is of the same kind as takes place in the case of hydrogen chloride. Determinations of the strengths of acids, &c., may then be made. In a similar manner the volumetric estimation of silver may be taught and the percentage of silver in coinage and other alloys determined.

Such a series of quantitative exercises as the foregoing, when carried out *before* and to a considerable extent *by* the pupils, undoubtedly affords mental discipline of the very highest order, and is effective of good in so many ways that the value of such teaching cannot be overestimated. The failure to grasp quantitative relationships which examiners have so frequently to deplore is without question largely, if not alone, due to students' entire ignorance of the manner in which such relationships have been determined. Moreover, the appreciation by the general public of the principles on which quantitative analysis is founded would undoubtedly be directly productive of good in a multiplicity of cases.

Stage VI.—*Studies of the Physical Properties of Gases in Comparison with those of Liquids and Solids. The Molecular and Atomic Theories and their Application.*

A series of quantitative experiments on the effect of heat on solids, liquids, and gases should now be made, and these should be followed by similar experiments on the effect of pressure: the similar behaviour of gases, and the dissimilar behaviour of liquids and solids, is thus made clear. The condensation of gases is then demonstrated and explained, and also the conversion of solids and liquids into gases, and the dependence of boiling-point on pressure and temperature. Regnault's method of determining gaseous densities is studied, and the method of determining vapour densities is illustrated. The molecular constitution of a gas is now discussed; the phenomena of gaseous and liquid diffusion are studied

and a brief reference is made to the kinetic theory of gases; then Avogadro's theorem is expounded and applied to the determination of molecular weights; and eventually the atomic theory is explained, and the manner in which atomic weights are ascertained is brought home to the pupils. The use of symbols must then be taught. Finally, the classification of the elements in accordance with the periodic law should be explained.

It is all-important that at least a large proportion of the experiments in each of the stages should be made by the pupils; but even if this were not done and the lessons took the form of demonstrations, much valuable instruction might still be given.

The majority of pupils probably would not proceed to the fifth and sixth stages; but those who perforce must terminate their studies without gaining any knowledge of chemical philosophy should unfailingly be led to make a few simple quantitative experiments: for example, to determine silver volumetrically, and the method of determining the composition of water and chalk gas should be demonstrated in their presence: and it may be added that if only the examples in Stages I. and II. and Problems I. to V. of Stage III. were thoroughly worked out, most important educational training would be given and much valuable information as to the nature of common phenomena would be gained.

The complete course would undoubtedly take up considerable time, but so does a satisfactory mathematical or classical course of study, and it is absurd to suppose that useful training in science is to be imparted in a few months. If instruction be given in the manner suggested at all generally, it will be necessary, however, to modify the present system of testing results. Pupils could not be expected to pass at an early age examinations such as are at present held, and awards would have to be based chiefly on an inspection of the classes at work, and of note-books, and on *vivâ voce* questioning. But all are agreed that the present system of payment on results tested by a terminal examination is a most unhealthy one, and that a more rational system *must* be substituted for it. I may suggest that if members of the staff of science colleges, such as are now established in so many towns, could be appointed *supervising inspectors*, whose duty it would be to advise teachers in schools and *occasionally* to inspect the teaching in company with the permanent inspector, it would be possible to secure the assistance of a body of men who are in touch with scientific progress and conversant with the improvements which are being effected. A man who "once an inspector is always an inspector" of necessity must get into a rut, and will escape from the wholesome leavening and rousing influence which is always more or less felt by those whose office it is to follow the march of scientific progress.

It should also here be pointed out that the great majority of the experiments and exercises described may be carried out with very simple apparatus and with slight provision in the way of special laboratory accommodation. In but very few cases is there any production of unpleasant smells or noxious fumes. It is, in fact, a mistake to suppose that an elaborately fitted laboratory is in every case essential for successful teaching: much might be done in an ordinary schoolroom provided with a demonstration bench for the use of the teacher, a draught closet over the fire-place, a sink, a raised table for balances (raised so that the teacher might see what was going on), a cupboard for apparatus, and a long narrow bench provided with gas burners at which, say, twenty pupils might stand ten a side. At present the Science and Art Department will not recognise "practical chemistry" unless it be taught in a laboratory fitted up in a certain specified manner, and their regulations are such as to enforce the provision of expensive laboratories in all cases where it is desired to obtain the grant. If greater latitude in fittings were allowed, more attention being paid to the character of the work done and less to the tools with which it is accomplished, probably much less money would be wasted by inexperienced school authorities in providing special laboratories, and there would be much greater readiness displayed to enter on the teaching of experimental science. The course which has been sketched out is one which doubtless might well be modified in a variety of ways according to circumstances. Thus many simple exercises in mechanics, in addition to those directly mentioned, might be introduced into Stage II., and the mechanical properties of common materials might be somewhat fully studied at this stage in districts where engineering trades are largely established, and where such knowledge would be specially valuable. In like manner the physical effects of heat on substances might be studied in Stage III. instead of Stage VI. And there are other chemical problems and simple exercises besides those described which might be substituted for some of them or included in the course.

Probably, however, it would be found undesirable, if not impossible, as a rule, to continue the teaching of chemistry proper much, if at all, beyond the stage indicated in this scheme. Other subjects will have a prior claim should it ever be deemed essential to include in a comprehensive scheme of school education the elements of the chief physical and physiological sciences; it certainly is of primary importance to introduce at as early a period as possible the conception of energy, and to explain the mechanical theory of heat, so that later on it may be possible to discuss the efficiency of heat and other engines; and, until the laws of the electric current are understood, the subject of chemical change can never be properly considered.

In many cases, where it is convenient or desirable to continue the chemical studies, it probably will be advantageous as a rule that they have reference to specific (local) requirements—*e.g.*, to agriculture in schools in agricultural districts; to food materials and physiology in the case of girls especially, &c. But in any case more consideration must be paid in the future in schools where chemistry is taught to educational requirements—the teaching must have reference to the requirements of the general public; and it must be remembered that the college, not the school, is the place for the complete study of a subject.

(To be continued).

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—We have read with great interest the article appearing in the Chem. News, vol lx., p. 184. Permit us to correct herewith some erroneous statements which it contains.

The quantities actually used at Wimbledon per 1000 gallons are about 6½ lbs. of lime and about 6½ ozs. of herring brine.

Blyth's experiments, to which you refer and which are in accord with those of Koch (see *Mittheilungen aus dem Kaiserlichen Gesundheitsamte-Berlin*), do not traverse Dr. Klein's results or our claim.

We do not claim any disinfecting power for amines, but for a new reagent evolved therefrom by the action of the lime.

When we characterised other sludges as a nuisance, we meant, of course, only *wet* sludges; we are not aware of any other process which claims, and can prove, for its *wet* sludge that it is inoffensive.

We shall be obliged by your inserting this in your next issue.—Yours &c.,

Hugo Wollheim.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 12, September 16, 1889.

Evaporation-Heat of Carbonic Acid near the Critical Point.—E. Mathias.—A mathematical paper, not susceptible of useful abridgment.

Supplementary Thermic Data.—J. Ossipoff.—The author determines the hydration-heat of maleic anhydride and the neutralisation-heats of the maleic and fumaric acids.

Thermic Formation of the Salts of Phenylendiamines.—Leo Vignon.—The author gives thermochemical data yielded by the meta- and ortho-compounds.

Alcoholic Fermentation of Honey and the Preparation of Mead.—G. Gastine.—Solutions of honey do not readily undergo the alcoholic fermentation, even in the most favourable circumstances. The author overcomes this difficulty by adding to the honey the mineral salts necessary for the growth of the ferment, and a small quantity of bibasic ammonium phosphate and neutral tartrate. The solutions of honey should first be sterilised by boiling and closed with a plug of wadding.

Journal de Pharmacie et de Chimie. Series 5, Vol. xx., No. 2.

Molecular Combinations of Camphor. — P. Cazeneuve.—Already noticed.

Action of Borax upon the Polyatomic Alcohols and Phenols. — A. Lambert.— Borax may serve as a reagent for showing if a sugar possesses the primary function, and if a polyatomic phenol belongs to the ortho-series.

Rapid Determination of Saccharine Matter with a Decinormal Cupro-potassic Solution.—J. E. Politis.—The difficulty in determining sugars with Fehling's liquid is the detection of the end of the process. The author uses a decinormal Fehling's liquid in excess, and after reduction he determines the excess of copper by De Haen's method with potassium iodide and sodium thiosulphite.

Detection of Chicory in Coffee. — M. Baumert (*Journal de Pharm. de Lorraine*), Karz.— The author founds his process on the excess of chlorine in chicory, which is nine times greater than in coffee. He incinerated 25 grms. of genuine coffee, treated the ash with an alkali, and lixiviated it with water slightly acidified with nitric acid. The liquid required 7·5 c.c. of normal silver nitrate. The same quantity of chicory requires 70 c.c. of the solution (1 c.c. represents 1 milligrm. of chlorine).

MISCELLANEOUS.

The Utilisation of Cow's Milk.—As hitherto no experiment has been made as to the utilisation of cow's milk by adult persons the author made an investigation of this kind on a healthy powerful labourer. This man took for three days daily 3 litres of milk, which he consumed without repugnance and which occasioned him no inconvenience. The milk and the excreta were analysed. In spite of the large quantity of milk the body was not in equilibrium as regards nitrogen, since the milk contained only 39·84 grms. nitrogen, whilst 61·51 grms. were expelled in the excretions. The experiment proved that of all animal and most vegetable foods milk is least completely utilised in the body of the adult. Children utilise it better.—*Zeitschr. f. Biologie* and *Chemiker Zeitung.*

Action of Soaps and Fatty Acids in the Animal Body.—The author shows that on the injection of small doses (0·08 to 0·09 grm. per kilo. of body-weight) into the blood of rabbits, the beats of the heart, after a short transitory acceleration, became slower and feebler, whilst the consumption of oxygen and the excretion of carbon dioxide fell to from one-half to one-fourth of their value as previously ascertained. On stronger injections (0·14 grm.) the heart beat still more slowly, and finally came to a stand. Check experiments with volatile fatty acids showed that of them doses from five to seven times larger did not weaken the action of the heart. Further experiments on the action of the soda soaps upon dogs showed that these soaps had more paralysing effect upon the heart the more rapidly they were introduced into the circulation. — *Central-Blatt. Med. Wissenschaft* and *Chemiker Zeitung.*

The Principal Cause of the Attenuation of the Poison of Rabies.—According to the view of Pasteur dry air is the chief cause of the attenuation of the virus of rabies. M. Protopopoff has demonstrated that this virus may be preserved in a pure state if a piece of the spinal marrow of a rabbit which has died of rabies is placed in glycerin broth which has been sterilised in the steam apparatus of Chamberland. The poison of rabies very quickly loses its poison property even in glycerin broth if it is kept at a higher temperature. He has proved that the attenuation of the virus in the system of preserving the vaccine for rabies in glycerin broth is in direct relation to the temperature, and that the latter is the sole cause of the attenuation of the poison on Pasteur's principle.—*Central-Blatt f. Bacteriologie* and *Chemiker Zeitung.*

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See opinion *Electrical Review*, October 21.

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BOY COURT, LUDGATE HILL, LONDON, E.C.

THE CHEMICAL NEWS.

Vol. LX. No. 1561.

THE MANUFACTURE OF ALUMINIUM FROM CRYOLITE.*

By Professor P. PHILLIPS BEDSON, D.Sc.

At the last meeting of the British Association in this city the manufacture of aluminium formed the subject of a paper read before this Section by our President, Sir Lowthian Bell, in which an account was given of the method practised at the Washington Chemical Works, where the manufacture of aluminium had then been in operation for some three and a half years. Shortly afterwards this interesting manufacture ceased to be a local industry, but the present year has witnessed the return of this manufacture to the Tyneside, where it promises to make a home for itself. These facts in themselves would form a sufficient excuse for laying before the members of this Section an account of this industry, but inasmuch as the method of manufacture at present practised on the Tyne is one of an entirely novel character, an apology for a description of such a process is scarcely needed. For whilst the process described by Sir Lowthian Bell in the paper, already referred to, is the one due to H. St. Claire Deville, viz., that dependent on the decomposition of the double chloride of aluminium and sodium by metallic sodium, which is also used at the Oldbury Works, Birmingham, and recently described by Sir Henry E. Roscoe, the method described in this paper is dependent on the decomposition of the mineral cryolite, a double fluoride of sodium and aluminium, by metallic sodium. The credit of the successful application of this decomposition to the manufacture of aluminium on an industrial scale is due to Professor Netto. To the kindness and courtesy of Professor Netto I am indebted for the details of the methods employed, as also for the opportunity of witnessing their practical application at the works of the Alliance Aluminium Co., Limited, Wallsend.

The various processes which have been suggested for the manufacture of aluminium since the discovery of this metal; and which have, in any way, proved to be of practical value, may be summarised as follows:—

(1). *Electrical Methods.*

a. The electrolytic decomposition of halogen compounds of aluminium in a fused state.

b. The electrolytic decomposition of oxygen compounds of aluminium.

c. The electro-thermal decomposition of oxygen compounds of aluminium in presence of carbon.

(2). *Metallurgical Methods.*

By the decomposition of molten halogen compounds of aluminium by means of metals having a strong affinity for the halogen elements, such as sodium, potassium, or magnesium.

The only processes capable, in practice, of yielding a pure and unalloyed metallic aluminium are the metallurgical, of which there are two.

The older of these is Deville's method. This mode of producing aluminium necessitates first, the manufacture from a suitable natural aluminiferous material of hydrate of alumina. Secondly, the conversion of this hydrate of alumina into the double chloride of aluminium and sodium, $AlCl_3(NaCl)_3$, which conversion is effected by submitting a mixture of the hydrate of alumina, carbon, and common salt, heated at a high temperature in retorts to the action of chlorine, condensing, and collecting the double chloride produced in suitable vessels. The third series of operations is the decomposition of the double chloride so obtained by means of metallic sodium.

The second metallurgical method is that due to Professor Netto, in which the mineral cryolite, a compound similar in chemical constitution to the chloride of aluminium and sodium, from which it differs in containing the element fluorine, instead of chlorine, its composition being expressed by the formula $(NaF)_3AlF_3$, is substituted for the double chloride of aluminium and sodium, and which, after admixture with suitable fluxes, is decomposed by metallic sodium. Although it has been known since 1855 that cryolite can be decomposed by sodium so as to yield its aluminium in the form of the metal, an observation made by the late Dr. Percy and Heinrich Rose, still it is only within the last two years that these facts have remained anything more than a matter of purely scientific interest. Many attempts have been made to utilise this reaction in practice, but hitherto the difficulties associated with its application have proved too great.

Amongst these difficulties may be enumerated, first those arising from the high melting-point of cryolite itself. The temperature at which this mineral melts is such that when metallic sodium and cryolite are intimately mixed, and the mixture heated to the point needed in order that the sodium may act upon the cryolite, the greater portion of the sodium is volatilised before it has performed its work. The second main hindrance to the use of cryolite arises from the fact that this mineral is always associated with quartz or other siliceous minerals, which, by reason of their physical properties, it is impossible to separate by any mechanical means. As these compounds also are decomposed with the fluoride of aluminium by the sodium, and in such a way as to yield silicon, the latter unites with the aluminium produced, in fact is concentrated in the metal obtained, and materially affects its physical properties and consequent utility in the arts. These difficulties have been successfully overcome, the first by fusing the cryolite before introducing into it the metallic sodium, which is effected by means of a special appliance, the sodium being submerged in the molten liquid; thus loss by volatilisation and its combustion is prevented.

Manufacture of Aluminium.

In practice the decomposition of cryolite by metallic sodium represented by the equation—

$$3Na+(NaF)_3AlF_3=6NaF+Al$$

is effected in two ways. On the large scale, a charge consisting of 200 lbs. of cryolite, mixed with 200 lbs. of salt, is melted in a reverberatory furnace. The fusion of this mixture requires about an hour and a half for its completion; the molten charge is then run into an iron converter which has been previously warmed. A block of sodium weighing about 5 lbs. is next thrown into the molten mass and immediately submerged by means of a "dipper" worked by two men. The "dipper" consists of a long iron bar, in the middle of which, and at right angles to it, is a second iron rod, to the free end of which is attached a circular piece of sheet iron, slighly concave, and studded throughout with holes. This circular piece of iron fits into the converter, and is worked up and down by a man stationed at each end of the long bar. Immediately on the sodium being brought into contact with the molten cryolite and salt, it is covered by the dipper and slowly depressed through the mass. This operation is repeated until the requisite quantity of sodium has been used, which for such a charge would be some 40 lbs. The introduction of the sodium is attended by a violent reaction, and at the commencement of the "dipping" the temperature rises and a considerable ebullition takes place, accompanied by production of flame and dense white fumes, consisting chiefly of sodium fluoride.

* Read before the British Association, Section B, Newcastle Meeting.

the dipping proceeds the mass grows darker and the reaction attending the introduction of the sodium less violent. When the required quantity has been introduced the bulk of the slag is poured off by tilting the converter, which is suspended on trunnions, into a large iron pot, and the last portion, containing the aluminium, is poured into a small iron vessel, in which, on cooling, the aluminium is found collected together in a mass. The separation of the greater bulk of the slags in this way is essential to the successful extraction of the aluminium, since, if the whole mass were allowed to cool, the separated aluminium would gradually dissolve up again in the slags.

A notable feature is the short time required to effect this decomposition of the cryolite by sodium, which does not allow of any loss by volatilisation of the sodium, nor is there any opportunity for a loss by its combustion, since it is always covered by the molten liquid, and thus protected from the action of the air. By this comparatively simple method of manipulation, what might otherwise be a very dangerous operation is effected without any great risk of injury to the workpeople, who are also protected against accident by special gloves and masks.

Working in this manner, and with a pure cryolite, the aluminium obtained would be practically pure, and from the amount of cryolite mentioned above the weight of aluminium produced would be about 10 lbs., requiring about 40 lbs. of sodium for its production. The slags produced contain about 40 per cent of sodium fluoride, 43 per cent of sodium chloride, 15 per cent of cryolite, and some alumina, together with about 0·75 per cent of metallic aluminium in a fine state of division scattered throughout the mass.

The mention of the finely-divided aluminium brings to mind one of the difficulties associated with the manufacture of this metal, which, by reason of its lightness, does not sink through the slag produced, as is the case in the production of other metals.

The second difficulty attending the use of cryolite as a source of aluminium is due to the impurities contained in native cryolite, impurities varying in amount from 1 to 3 per cent. The influence of these impurities is overcome by making use of the fact that the chief of these, viz., the compounds of iron and silicon, are reduced by sodium before the fluoride of aluminium is attacked. To this end the molten mixture of cryolite and flux is dipped with one-third of the sodium required for its decomposition; in this manner the iron and silicon are precipitated with some aluminium, and the liquid poured off from this into another hot converter; this again is treated with the remainder of the sodium needed. With an ordinary cryolite, by this method of "double dipping" a metal containing from 98 to 99 per cent of aluminium is easily obtained. For special classes of aluminium of the very best manufacture working in crucibles is adopted, since, in this way, a better control of the liquid mass of cryolite and flux is obtained, as the crucible stands in the furnace during the whole operation of "dipping." In such cases the practice of "double dipping" is always resorted to. The crucibles employed are made of fire-clay and manufactured by Messrs. Morgan, of London; these are heated in furnaces built in the floor, similar to those employed by steel melters; the fuel used is coke. The introduction of the sodium into the molten mass in the crucibles is effected by fastening a block of sodium to an iron rod, and covering it with a circular piece of metal provided with holes, and also a slit in which the rod fits. The circular piece of metal is attached to a rod of iron, which serves to keep the cover over the sodium. By the aid of these appliances the sodium can be introduced into the molten liquid under conditions similar to those in which it is used in the working on the large scale.

I am led to understand that the Alliance Aluminium Co., which uses Prof. Netto's method, classify the aluminium produced in the above-mentioned manner as follows:—

Class AA, produced in crucible and by "double dipping," 98·5—99 per cent aluminium.

Class A, produced in converter and by "double dipping," 97—98·5 per cent of aluminium.

Class B, produced in converter and by single dipping, 95—97 per cent of aluminium.

Class C, produced in converter and by "double dipping," being the first product of the "double dipping," 90—95 per cent aluminium.

Another point, and one of considerable interest in connection with the production of aluminium from cryolite is the composition and regeneration of the slags. These slags contain some 40 per cent of sodium fluoride, and also some ¾ per cent of metallic aluminium. Prof. Netto informs me that this metallic aluminium has been recovered from these slags by melting the slag with metallic copper, and producing in this way an aluminium bronze. From the slags, after treatment with metallic copper, cryolite can be reproduced by heating the slags together with aluminium sulphate, in suitable proportions, and extracting the sodium sulphate found by a subsequent treatment with water. The reaction upon which this regeneration depends is expressed as follows:—

$$12NaF + Al_2(SO_4)_3 = 3Na_2SO_4 + 2Na_3AlF_6.$$

This simple method of utilising the slags formed for the production of cryolite—a cryolite which in many ways is purer than native—places the manufacture of aluminium from cryolite on a better footing than its production from the double chloride of sodium and aluminium.

The following are the amounts of the various materials required for the production of one part by weight of aluminium:—

12	parts	by weight of	cryolite.
12	,,	,,	common salt.
20	,,	,,	coal.
3	,,	,,	sodium.

At the same time there are produced 20 parts by weight of slags containing 40 per cent of sodium fluoride, 15 per cent of unreduced cryolite, 43 per cent of salt, a small proportion of alumina, and some ¾ per cent of finely-divided aluminium.

From the above it is evident that the production of aluminium by this method is largely dependent upon the cheapening of the manufacture of sodium, of which metal from 3—4 parts are required for the manufacture of 1 part of aluminium, the theoretical proportion being 2·5 of sodium to 1 of aluminium. Consequently, in recent years, many efforts have been made to reduce the cost of sodium production and improve the existing methods. Of all these attempts the most successful have been those in which caustic soda has been substituted for the carbonate of soda. The use of caustic soda in the manufacture of sodium is dependent on the observation first made by Curaudau, shortly after the discovery of metallic sodium by Davy, that caustic soda is decomposed when heated with carbon, and metallic sodium produced. The decomposition may be represented by the following equation—

$$2NaOH + C_2 = Na_2 + 2CO + H_2.$$

The main difficulties attending the use of caustic soda in this way are those arising from its easy deliquescence, and secondly, from the ease with which it passes, when fused, into a thin mobile liquid, which prevents the permanent establishment of an intimate admixture of the reducing agent. Inasmuch as the decomposition of the caustic soda by carbon takes place at a lower temperature than that of the carbonate, the cheapening of the production of sodium in this way has been found to be possible, despite the difference in price between the carbonate and caustic. The reaction, however, is not in reality as simple as the above equation would lead one to imagine, for a portion of the caustic soda is converted into carbonate of soda, which would require a higher tempera-

ture for its decomposition. The formula of carbonate of soda may be represented as follows:—

$$4NaOH + C_2 = Na_2CO_3 + Na_2 + 2H_2 + CO.$$

Castner has overcome one of the chief difficulties attending the use of caustic soda by weighting the carbon by previous fusion with metallic iron, but in heating this mixture the carbonate of soda produced, as represented by the equation above, serves to dilute the caustic soda, and necessitates the use of retorts or crucibles made of steel or wrought iron, in which the materials can be raised to a temperature sufficiently high to decompose the carbonate of soda and the caustic. Professor Netto has surmounted these difficulties by effecting the removal of the carbonate of soda, as it is produced, from the zone of decomposition, and he has, consequently, been enabled to make full use of the comparatively low temperature at which caustic soda is decomposed by carbon, and to utilise cast-iron retorts for this purpose. To this end fused caustic soda is allowed to flow in a carefully regulated stream over a mass of heated charcoal contained in a retort, the gaseous products pass through an opening in the top of the retort, and the sodium condenses and is collected in an iron pan; the undecomposed caustic soda and the carbonate of soda collect at the bottom of the retort, and are drawn off from time to time.

This method will perhaps be made more intelligible by a description of the plant employed. The retorts made of cast-iron are pear-shaped, and about three feet in height; at the bottom is a tubulus closed by a plug, and serving for the withdrawal of the slags. Fitting on to the top of the retort is a lid with three openings; one serves to convey the gases and vapours produced to the condensing apparatus; the second opening is used for the introduction of the charge of the reducing carbon; and the third, which is surrounded by a cup, is closed by a screw-valve, by which the flow of fused caustic soda can be regulated. The retort is supported on brick-work, and is surrounded by a circular furnace, in which coke is used as fuel. The heated gases are led away at the top of the retort, at a point below the lid, into a chamber in which is built an iron box, in which the caustic soda is melted by the heated gases from the furnace. The iron box is provided below with an aperture opening into a channel along which the liquid caustic soda is conducted to the cup on the lid of the retort. The opening in the iron box is also closed by a screw-valve, which further serves to regulate the supply of liquid caustic soda to the retort. Fitting on to the top of this iron box is another closed by a lid, and provided at one side with a slide, which can completely divide the upper box from the lower one, and thus prevent the solid caustic soda from falling suddenly into the fused mass below. The upper box having been filled with solid caustic soda it is then closed by the lid, and the slide gradually withdrawn to allow the solid caustic soda to fall into the vessel below, in which it is melted.

In this manner a portion of the caustic soda is decomposed and metallic sodium produced; the portion partially converted into carbonate collects at the bottom of the retort, and is drawn off from time to time, forming what is styled a soda slag. The soda slags can either be re-causticised or sold to paper manufacturers and others, and, in fact, find a ready sale.

Every twelve hours the process of sodium production is interrupted for a short time for the purpose of re-charging the retort with charcoal. Such a retort will yield 42 kilogrms. of sodium in a day, and will produce 750 kilogrms. of the metal before it is so acted upon as to necessitate a renewal.

The following are the amounts of the several materials required for the production of one part by weight of sodium:—

10	parts	of caustic soda
1·2	,,	cast-iron for the retorts
12	,,	coke
1·5	,,	charcoal for reduction.

At the same time nine parts of soda slags are produced, consisting chiefly of carbonate of soda and some caustic soda, containing about 60 per cent Na_2O.

In conclusion, I must express my great indebtedness to Professor Netto for the kind manner in which he has assisted me, in furnishing the information with which it has been possible for me to give an account of the latest Tyne-side industry. Further, I am indebted to Professor Netto and the Alliance Aluminium Company, of Wallsend, for the specimens and photographs illustrating the manufacture of sodium and of aluminium from cryolite.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 189).

Mineral acids considerably attack the ready-formed precipitate, even in presence of ammonia, and especially on the application of heat. The colourless acid solutions separate out the dissociated phosphomolybdate, neutralising the excess of acid. Nitric acid seems to act most slightly, hydrochloric acid more strongly, and sulphuric acid most of all.

The following experiment may prove how intense is the decomposition of the ready-formed precipitate by nitric acid, even in presence of ammonium nitrate:—

In a neutral solution of 0·010 grm. P_2O_5, 0·243 grm. MoO_3, and about 10 grms. NO_3NH_4, the phosphomolybdate was thrown down by a slight excess of nitric acid. A few drops of molybdate solution produced in the solution (the volume of which was about 50 c.c.) no trace of a precipitate; but after about 1000 mols. NO_3H (20 c.c. of the nitric acid used in an experiment already described) had been further added, and the whole had been heated nearly to a boil, there appeared again a precipitation with molybdic acid, until altogether 0·051 MoO_3 had been further added. The separation of the P_2O_5 required now about 21 per cent MoO_3 more than before, showing that in such a short time about one-fifth part of the precipitate had been decomposed by the acid. If the heating had been prolonged probably half the precipitate would have been destroyed.

Organic polybasic acids, oxalic or tartaric acid, and their salts decompose the precipitate in heat very readily. Their presence, as already intimated, hinders the re-union of the phosphoric and the molybdic acid under all circumstances.

The action of reducing agents did not come within the scope of the author's investigations.

Of all the substances above named the most suitable for washing the ammonium phosphomolybdate are faintly acidulated solutions of ammonium nitrate or chloride, both cold and warm, of which about five per cent in the washing water is sufficient; then follows acidulated solution of ammonium sulphate (five to ten per cent), as also dilute nitric or hydrochloric acid (one to two per cent), but these acids must not be left long in contact with the precipitate. For neutral washing, cold solutions (about five per cent) of neutral ammonium nitrate or chloride, or for rapid washing, ice-cold water. Water at common temperatures must be avoided, as even with the greatest care traces of the precipitate can scarcely be prevented from passing through the filter or becoming dissolved.

Such a small loss on washing with water is the cause why Hehner divides the weight of the residue by 28·5 in order to find the correct weight of P_2O_5.

7. *The Titration of Phosphoric Acid with Molybdic Acid, and that of Molybdic Acid with a Solution of Phosphoric Acid.*

In order that the quantity of P_2O_5 present may be correctly inferred from the quantity of MoO_3 consumed in precipitating the phosphoric acid, the quantity of nitric acid which co-operated in the formation of the ammonium phosphomolybdate must be known at least approximately.

This knowledge is acquired and the object is attained, so that at any moment a degree of acidity favourable to the formation of phosphomolybdic acid is present, by making the solution to be titrated neutral or very slightly acid, and to the solution of molybdic acid there is added at the outset not more and not less than the quantity of nitric acid most favourable for the formation of the phosphomolybdate in a neutral solution and for its rapid separation, *i.e.*, to 1 mol. MoO_3 about 3—4 mols. NO_3H, corresponding to 36—48 mols. to 1 mol. of the phosphomolybdate to be precipitated. After the formation of the precipitate the solution would contain only about 10—22 mols. of free nitric acid. It will be remembered that in a solution with this proportion of acid the influence of dissociation is imperceptible, and in such a one the mol. of P_2O_5 is thrown down quantitatively by 24 mols. MoO_3.

For the titration of small quantities of phosphoric acid the author uses with success:—

Ten grms. pure molybdic acid (or 12·262 grms. pure crystalline hexammonium heptamolybdate) are dissolved in an excess of dilute ammonia, the liquid is mixed with about 15 grms. NO_3H (*e.g.*, 39 c.c. nitric acid of sp. gr. 1·20) and diluted to 1 litre. It contains thus per mol. of neutral molybdate 3·43 mols. NO_3H, or per mol. of free MoO_3 1·43 mols. of free NO_3H, which suffice along with the ammonium phosphomolybdate precipitated in a neutral solution to leave an excess of about 15 mols. NO_3H (supposing that sulphates are absent).*

Of this solution there were consumed for the precipitation of 0·010 grm. P_2O_5, independent of the proportion of phosphoric acid in the liquid to be titrated (it contained about ten per cent of ammonium nitrate), from 24·3 to 24·5 c.c., that is the quantity of phosphoric acid theoretically required.

In titration the author proceeds as follows:—The neutral or slightly acid solution of phosphate, which does not need to contain in 100 c.c. more than 0·025 grm. P_2O_5, and which should not be more concentrated, is mixed with so much ammonium nitrate that in 100 c.c. it may contain 10—15 grms. NO_3NH_4, and is heated nearly to a boil. Small quantities of the molybdic solution—towards the end only drops—are run in until no further precipitate of ammonium phosphomolybdate appears. The presence or the absence of renewed precipitation is detected accurately and conveniently, and without filtering portions, as follows:—

Care must be taken by a suitable position of the Bunsen (or other burner) that the ascending current of the heated liquid is not in the front, but in that part of the vessel which is turned away from the observer, so that in those strata of the liquid which are nearest to the observer there is a slow downward movement which here effects a very gradual intermixture of the molybdic acid solution with the rest of the liquid. There is then placed close behind the vessel a piece of blue cobalt glass, so that its upper edge rises a few c.m. higher than the level of the liquid. If viewed against this glass the finest particles, the slightest traces of an incipient precipitate, are clearly apparent.

The molybdic solution is then let flow in along the front side of the vessel so that it may float upon the solution, which is specifically heavier. In the zone where the liquids mix there appears at once a dense pale yellow cloud, from which the precipitate, as it condenses, slowly *snows down*. The observer mixes, and whilst the precipitate subsides he removes the yellow stripes and coatings on the front side of the beaker, which would interfere with the observation of the phenomena, using a glass rod, the end of which is covered with a ring-formed piece of caoutchouc tubing. When the liquid has become sufficiently clear (which at first takes a considerable time, but becomes more rapid towards the end of the process) a little more molybdic solution is let flow upon the surface; after waiting a few seconds, until the precipitate has formed, the liquid is stirred and the process is continued in the same manner until the last drops no longer produce a cloudy zone. When, after adding 2 or 3 drops of the molybdic solution, there does not, in the course of half a minute, appear a faint stripe at that part of the side of the beaker where the drops entered the surface of the liquid, the precipitation may be regarded as complete. So long as this stripe is still visible (which is best seen along the upper edge of the meniscus if viewed from above at an angle of 45°) traces of phosphoric acid still remain in solution. This last character is especially important for the titration of small quantities of phosphoric acid.

The following examples show the accuracy which may be reached if all the precautions are observed:—

1. 0·00050 grm. P_2O_5 required for precipitation 1·260 c.c. MoO_3 solution. 0·0126 MoO_3 = 0·000518 P_2O_5.

2. 0·00025 grm. P_2O_5 required 0·598 c.c. molybdic solution. 0·00598 molybdic solution = 0·000246 P_2O_5.

3. 0·00040 grm. P_2O_5 required 0·972 c.c. molybdic solution. 0·00972 = 0·00040 P_2O_5.

The above mentioned molybdic solution keeps unchanged for months, even if exposed to frequent changes of temperature; less concentrated solutions deposit in time small quantities of molybdic acid; hence if it is desired to work with solutions containing a larger proportion of molybdic acid, there must be prepared a neutral titrated solution of molybdate and a titrated nitric acid, both being kept apart, and in the determination there must be used two burettes, or a kind of double burette, one tube of which contains the molybdic solution and the other the acid, from which each fluid is let flow alternately in proper proportions.

The method may be inverted and used successfully for the titration of molybdic acid by means of a solution of known value. In a solution of the right acidity 24 mols. MoO_3 are exactly precipitated by 1 mol. P_2O_5, whether the nitric acid is originally contained in the molybdic solution or it is introduced along with the phosphatic solution.

For practical purposes a neutral or slightly acid solution of molybdic acid is mixed with about 10 per cent of ammonium nitrate and titrated hot with a solution of sodium hydrophosphate, which contains, per mol. of P_2O_5, about 80 mols. NO_3H.

As it will be seen from the above, in titrating by the methods described, appreciable quantities of sulphates or other salts of polybasic acids would interfere, as also salts of monobasic organic acids. Polybasic organic acids and reducing agents must not be present. Small quantities of silica do not interfere. If appreciable quantities of salts of polybasic inorganic acids, such as sulphates, are present, the following expedient may be adopted:—

The faintly acid liquid to be titrated is first mixed with a known volume of the standard solution—say $\frac{1}{2}$ to $\frac{1}{4}$ of the total quantity required for precipitation—it is cautiously acidified with dilute nitric acid, until there is formed a permanent precipitate of ammonium phosphomolybdate and no longer increases, and the titration is then completed in the manner described above.

* Pure molybdic acid, free from phosphoric acid, can be quickly obtained in large quantities in a form readily soluble in ammonia by passing a strong current of air or steam through a boiling hot concentrated solution of ammonium molybdate. Ammonia is expelled from the solution, and a crystalline, snow-white, sparingly soluble molybdate is separated. By absorbing the moisture from the precipitate, washing in alcoholic water, repeated evaporation in case of need, solution in a little dilute ammonia, filtration, precipitation with alcohol, absorption of moisture, and oxidising ignition, a molybdic acid is obtained in the form of a dense white powder when cold.

In solutions rich in sulphate the phosphoric acid must be separated out in another manner and then re-dissolved in nitric acid for titration.

(To be continued).

WATER ANALYSIS.*

Having during the past two years given this matter our careful consideration, we beg herewith to submit the following report.

In order to ascertain the general feeling of chemists in this country on the subject, we have circulated the following series of questions amongst the leading water-analysts, upon whose co-operation the adoption of any uniform scheme must necessarily depend.

1. What is the system of recording the results of Water Analysis which you adopt?
   (*a*) For the Mineral matters.
   (*b*) For the Organic matters.
   (*c*) For the Gaseous matters.

2. Have you any objections, and if so what are they, to the use of a Decimal system—such as parts per million, per 100,000, per 10,000, or per 1000?

3. In recording the results of complete Analysis of the Mineral matters present in water, is it your custom to state the proportion of each individual Base and Acid as actually determined, or to combine the Bases and Acids so as to form salts?

4. Should it be your custom to combine the Bases and Acids, explain the principles by which you are guided in so combining them, and state what, in your opinion, are the advantages attaching to such combination.

5. If your present method of recording results is more or less influenced by special circumstances, such as the custom of professional Chemists generally, what other method of recording results would you yourself *select* as the most rational and the most convenient for universal adoption?

6. Would you support the adoption of the following method, recommended by the American Committee, of stating the constituents of a Mineral Water?—

"That the parts per thousand of each basic element, K, Na, Li, Ca, Mg, Fe'' (Fe_2), &c., be given, and of each acidic element, such as Cl, I, S, &c., that is combined directly with a basic element, or that may reasonably be supposed to be so combined, the rest of the acidic elements to be given in connection with all the oxygen of their salts, as usually written in our present empirical formulæ, as SO_4, CO_3, PO_4, &c."

From the answers we have received to the above questions, as well as from our own personal experience, we gather that there would be no reluctance on the part of British Chemists to adopt a uniform and rational scheme, but for the great difficulty of rendering such a method of statement popularly understood. Thus the majority of analysts employ the "*grain-gallon*" system of statement, as being the one most intelligible to their clients, and this system undoubtedly possesses certain advantages in the case of analyses for technical purposes, in which the analytical figures have to be applied to large volumes of water which in this country are almost invariably measured in gallons.

We find, however, a general readiness on the part of most analysts to adopt a uniform and prescribed system only to be departed from in special cases, and we are of opinion that it would be impossible to secure more than such a qualified consent to any one system.

Although there is but little possibility of directly influencing the custom of professional chemists in their private practice, we are of opinion that it is of great importance to urge upon water-analysts the desirability of adopting some uniform system in the case of such analyses as are communicated to scientific societies or other learned bodies, and which are therefore calculated to have a circulation in countries where the imperial gallon is not recognised, and if such uniformity could be secured there is but little doubt that the system would before long establish itself even in the case of analyses of a non-public character.

As regards the method of statement which would be most suitable for general use in such published analyses, we are of opinion

(1). That it should be on the decimal system, preferably *parts per million* (m.grms. per litre) or *parts per* 100,000, as *parts per* 1000 (grms. per litre) would too frequently give rise to fractional results. The special advantages attaching to "parts per 100,000" are that the figures or mineral waters are not inconveniently large, nor those or potable waters inconveniently small, whilst their conversion into grains per gallon is a very simple operation.

We cannot agree with the American Committee that different scales should be adopted for mineral and potable waters respectively, for such a dual system must, in our opinion, inevitably lead to confusion.

(2). We attribute the greatest importance above all to the clear statement, in every case, of the actual determinations made, and that all results derived by calculation should be sharply distinguished from those obtained by direct determination.

Thus we view with particular disapprobation the statement of the mineral ingredients combined as *salts*, unless accompanied by a clear account of the analytical data upon which this statement is founded.

(3). As regards the statement of the mineral ingredients, we have considered the method suggested by the American Committee, and which consists in recording the proportion of each metallic element (K, Na, Li, Ca, Mg, Fe'', Fe_2, &c.), as well as that of each electro-negative element (F, Cl, Br, I, S, &c.) contained in binary compounds, whilst in the case of oxy-compounds the electro-negative element is given as combined with the the whole of the oxygen (SO_4, PO_4, NO_3, CO_3, &c.), and we are of opinion that this arrangement is decidedly the most convenient for all purposes of calculation, although the absence of any recognised names for these acid-groups, as well as the prevailing custom of estimating the metallic elements in the condition of bases (K_2O, Na_2O, CaO, &c.) are undoubted objections to this system.

(4). That the amount of dissolved gases (O, N, CO_2, SH_2, &c.) may be most conveniently expressed either in cubic centimetres per litre or in volumes of gas per 100 volumes of water, the latter being the more general practice in this country.

The system of statement which we wish to recommend will be most readily understood from the following form for a complete analysis:—

Results of Analysis Expressed in Parts per 100,000.

Potable Water:—

Total solid matters	(*a*) In suspension ..	
	(*b*) In solution ..	
Organic carbon		
Organic nitrogen		
Oxygen consumed, as indicated by decolouration of permanganate..		
Ammonia expelled on boiling with sodium carbonate		
Ammonia expelled on boiling with alkaline permanganate		
Nitrogen as nitrates and nitrites		
Chlorine..		
Hardness	Temporary	
	Permanent	
	Total,.	

* Report of the Committee, consisting of Professors Dewar, E. Frankland, Percy F. Frankland (Secretary), and Odling, and Mr. Crookes, appointed to confer with the Committee of the American Association for the Advancement of Science with a view of forming a uniform system of recording the results of Water Analysis. Read before the British Association, Section B, Newcastle Meeting.

Mineral Water :—

Carbonate of lime ($CaCO_3$)	
Carbonate of magnesia ($MgCO_3$)	
Carbonate of soda (Na_2CO_3) (calculated from residual alkalinity after boiling and filtering off precipitated $CaCO_3$ and $MgCO_3$)	
Total calcium (Ca)	
Total magnesium (Mg)	
Total potassium (K)	
Total sodium (Na)	
Iron (ferrous) (Fe")	
Iron (ferric) (Fe_2)	
Sulphuric radical (SO_4)	
Nitric radical (NO_3)	
Nitrous radical (NO_2)	
Phosphoric radical (PO_4)	
Silicic radical (SiO_3)	
Chlorine (Cl)	
Bromine (Br)	
Iodine (I)	
Sulphur as sulphide (S)	

Dissolved Gases.

Cubic Centimetres of Gas at 0° C., and 760 Millimetres in 1 Litre of Water.

Carbonic anhydride (CO_2)	
Oxygen (O)	
Nitrogen (N)	
Sulphuretted hydrogen (H_2S)	

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 196).

WITH the object of presenting in an available form information as to the position occupied by chemistry in Board and other Public Elementary Schools, which are controlled either by the Education Department, Whitehall, or the Science and Art Department, South Kensington, the Committee now present a report on the subject which has been prepared by Professor Smithells. A consideration of this statement will show that, as in the higher grade public schools, with which the Report of the Committee last year was chiefly concerned, the condition of the teaching in public elementary schools is far from satisfactory. As a rule chemistry is not taught on the proper lines. The pupils frequently receive the same kind of instruction in chemistry as they would at a later stage if they were preparing for a professional or technical career; consequently the subject has failed to provide that mental education which it should be the main object of elementary teaching to develop. It appears, too, that in many of these schools physical science has not hitherto been regarded as a necessary part of the educational scheme. It is essential that this state of affairs should be altered, and that physical science should occupy a more favourable position in the Education Code, and that its teaching should be more thoroughly controlled.

It is to be hoped, also, that the Education Department, as well as the Science and Art Department, South Kensington, will take steps to arrange a more efficient mode of inspecting science teaching than that at present in vogue, which can only be regarded as satisfactory from a purely statistical standpoint. Under the present system little or no control can be exercised over the science teaching, since the Whitehall Inspectors are, as a rule, not qualified to form an opinion as to its value. There would seem to be no difficulty in obtaining the services of properly qualified persons to act as additional inspectors for the purpose of reporting on the character of the science teaching. It is probable that many of the professors and lecturers in University Colleges, and other educational institutions, might be willing to take part in such inspection, and it would thus become possible to maintain a high standard of excellence in the teaching.

*The Teaching of Chemistry in Public Elementary Schools.**

Drawn up by Professor SMITHELLS.

In view of the rapid increase in the teaching of chemistry in connection with public elementary schools likely to take place, chiefly on account of the establishment of the so-called "Higher Grade Board Schools," and in view of the strenuous attempt that is being made to extend the teaching of science subjects by a separate Act dealing with technical instruction, it seemed of importance to prepare a short statement indicating the position occupied by chemistry in our state-aided elementary schools. Since the chemical teaching in such schools is practically dominated by the syllabus of the Education Code and of the Science and Art Department, any improvements or suggestions the central authorities at Whitehall or South Kensington could be induced to accept would at once take effect throughout public elementary schools dealing with four and a half millions of children, or between one-sixth and one-seventh of the total population.

The following statement deals with the conditions under which chemistry is taught in Voluntary and Board Schools, and with the extent of such teaching, in England and Wales only. Notes are added with reference to chemistry teaching under the Scotch Edacation Department, and to other matters relating to the main question.

The Education Code.—The subjects of instruction in the Education Code are divided into three classes:—

1. ELEMENTARY OR COMPULSORY SUBJECTS.—Reading, Writing, and Arithmetic (and Needlework for girls).
2. CLASS OR OPTIONAL SUBJECTS.—English, Geography, Elementary Science, History, Singing, or other graduated subject approved by the Inspector.
3. SPECIFIC SUBJECTS.—Algebra, Euclid and Mensuration, Mechanics, Chemistry, Physics, Animal Physiology, Botany, Principles of Agriculture, Latin, French, Domestic Economy, and other subjects approved by the Inspector.

All schools must take the elementary subjects in all the standards.

Not more than two class subjects may be taken, one being English. (In the case of girls the second class subject must be needlework unless taken under the head of elementary subjects).

The specific subjects are only to be taken in the upper classes of a school, viz., in Standards V., VI., and VII.

There is in the Code as it stands the possibility of an excellent course of instruction in elementary chemistry. It would really begin in the infant school with enlightened object lessons and kindergarten work, then in the elementary school proper it could be continued in the first four standards as the class subject "elementary science," lastly, in the V., VI., and VII. Standards as the specific subject chemistry.

The teaching in the infant schools is not circumscribed by detailed schedules or individual examination, and is admittedly the most satisfactory part of our educational system.

The schedule for elementary science as a class subject is as follows:—

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

* *I.e.*, in Voluntary and Board Schools receiving grants from the Education Department under the Education Acts.

	Standard I.	Standard II.	Standard III
III. Elementary Science. A progressive course of simple lessons on some of the following topics, adapted to cultivate habits of exact observation, statement, and reasoning.	Common objects, such as familiar animals, plants, and substances employed in ordinary life.		

Standard IV.	Standard V.	Standard VI.	Standard VII.
A more advanced knowledge of special groups of common objects, such as— (*a*) Animals or plants, with particular reference to agriculture. (*b*) Substances employed in arts and manufactures. (*c*) The simpler kinds of physical and mechanical appliances, *e.g.*, the thermometer, barometer, lever, pulley, wheel and axle, spirit level.	(*a*) Animal or plant life. (*b*) The chemical and physical principles involved in one of the chief industries of England, among which agriculture may be reckoned. (*c*) The physical and mechanical principles involved in the construction of the commoner instruments, and of the simpler forms of industrial machinery.	The preceding in fuller detail.	The preceding in fuller detail.

Chemistry as a specific subject taken by boys in the V., VI., and VII. Standards is divided into three "stages" as follows, each stage representing one school-year's work:—

Stage I.	Stage II.	Stage III.
Elementary and compound matter. Illustrations of combination and decomposition in such bodies as hydrochloric acid, water, oxide of mercury, and rust of iron.	Preparation and properties of the common gases, such as oxygen, hydrogen, nitrogen, and chlorine. The chemical character and constituents of pure air and pure water, and the nature of the impurities sometimes found in both. Effects of plants and animals on air.	The properties of carbon and its chief inorganic compounds. Differences between metallic and non-metallic bodies. Combination by weight and volume. The use of symbols & chemical formulæ.

Any *further teaching* of chemistry than the above would not earn Government grants from the Education Department, but might be provided by school managers in extra classes or in a so-called Higher Grade School by money from the school funds or the rates (according as it were a Voluntary or Board School) and by means of grants obtained from the South Kensington Science and Art Department under conditions to be subsequently explained.

Inspection and Grants.—The teaching of the science in all stages would be subject to the inspection of one of H.M. Inspectors of Schools, on whose annual report the Government grant would be awarded. The examination, conducted once a year, in the elementary science is oral, and may be conducted as the Inspector likes. If the class is reported "fair" a grant of 1s. per head is allowed, if "good" 2s., and besides this the quality of work done in the class subject is considered in awarding the "merit grant," *i.e.*, a grant awarded to the school on the general merits of the organisation, teaching, and discipline, 1s., 2s., or 3s., according as it is "fair," "good," or "excellent."

In 1887-8, 25,000 out of 4,500,000, *i.e.*, 1 in 180, children in schools took this subject.

The teaching of chemistry as a specific subject is also under the control of H.M. Inspectors, who award a grant of 4s. on each pupil who passes at the annual written examination. The performance in specific subjects also counts in awarding the merit grant.

Teachers and Apparatus.—The teachers in the earlier standards (including elementary science) are the usual school teachers, and have not necessarily any qualification of a scientific kind.

The inspectors have instructions to ascertain that teachers of *specific* subjects have received training in a training college or have passed some public examination. The Department recommends the "peripatetic" system of science teaching by a "demonstrator," in which either the demonstrator visits the schools in rotation, or the pupils from the different schools attend a central laboratory for science instruction. This system has been adopted with success in several large towns, including London, Liverpool, Manchester, Birmingham, and Leeds.

There is no stipulation in the Code for apparatus or experimental illustration, this being a matter for the school managers, subject to the criticism of the inspectors.

Statistics.—The following are statistics as to the teaching of chemistry in elementary schools as a specific subject under the Whitehall Code for the year 1887-8:—

	Total No. examined.	Passed.	Per-centage.	1st stage.	2nd stage.	3rd stage.
Voluntary schools	453	327	72·2	181	127	19
Board ,,	1035	750	72·5	409	295	46
Total..	1488	1077	—	590	422	65

	Average number of scholars in attendance in all subjects.	Proportion taking chemistry (specific).
Voluntary schools ..	2,216,854	about 1 in 5000
Board schools	1,327,710	,, ,, 1280

The proportion taking chemistry in Board schools is thus about four times that in Voluntary schools.

Chemistry as a Science Subject.—The preceding statements apply only to teaching under the Whitehall Education Department. The greater part of the chemistry teaching is carried out under the Science and Art Department, South Kensington. This is done in virtue of a regulation of that Department, whereby pupils in elementary schools receiving aid from the Whitehall Education Department may be "registered" in a science subject provided that they have passed Standard VI. of the Code and are taught by a duly qualified teacher. Such teacher must have obtained a first class in the advanced stage of the May examinations of the Science and Art Department, or have obtained some qualification deemed equivalent by the Department.

Pupils who have passed Standard VI. may thus form a class under the Science and Art Department, and present themselves at the usual May examinations in chemistry.

For every pass in the elementary or advanced stage a payment of £2 for a first class and £1 for a second class is made, subject to a deduction of 4s. if the same pupils have within the previous six months been examined and have obtained grants through the Whitehall Department for chemistry as a specific subject.

For honours £4 and £2 for a first and second class, respectively, are granted.

In practical chemistry the following grants are made:—

£2 and £1 for first and second class elementary respectively
£3 „ £2 „ „ advanced „
£4 „ £3 „ „ honours „

The conditions are:—

(*a*). That the teacher is qualified as above.
(*b*). That he has given at least 28 lessons during the session.
(*c*). That each candidate has received 20 lessons.
(*d*). That the candidate does not present himself in more than two subjects.

Stringent conditions are also made as to laboratory accommodation and the provision of apparatus, and grants are made for these purposes.

The teaching is under the inspection of the South Kensington inspectors, who are only four in number. They are assisted by "acting inspectors," consisting of officers of the Royal Engineers, who may inspect classes in the neighbourhood where they are for the time stationed. Such inspection is, however, as a rule, merely "statistical" as to apparatus and laboratory fittings.

The syllabus of the examinations which regulate the teaching are too well known to need repetition here. They have been much improved in recent years by the creation of an "alternative first stage," consisting of a course of chemistry of common things.

An outline of suitable experiments for illustrating the courses, drawn up by Sir Henry Roscoe and Dr. Russell, is issued by the Department for the guidance of science teachers.

Organised Science Schools.—The teaching of chemistry in elementary schools is further influenced by the Science and Art Department by means of "organised science schools." Under the regulations of the Department the scholars of an elementary school (provided that it is not receiving aid from the Whitehall Department on their account) may be formed into an organised science school. For this purpose a course of purely scientific instruction (with the addition of drawing) is laid down. The course includes substantial instruction in chemistry.

For the pupils of such schools who register 250 attendances on the full course, and pass in one subject proper to each year, a capitation grant of 10s. is made in addition to what may be earned at the usual May examinations. Payments are not made for more than four years. The conditions are somewhat different for evening schools.

"Organised science schools" exist in some large towns, as Birmingham, Manchester, Leeds, Brighton, and Middlesborough, the total number in the country being twenty-three.

Statistics.—The following statistics show the number of pupils receiving instruction in chemistry in classes registered under South Kensington, and the number of such who are also studying the subject in public elementary schools.*

	Total number of individuals registered under South Kensington.	Total number of scholars of public elementary schools registered under South Kensington.
Inorganic (theory)	14,241	8202 (in 134 schools)
Inorganic (practical) ..	6,155	
Organic (theory)	1,244	
Organic (practical)	926	
Total taking theoretical, inorganic, and organic	15,485	8202

Taking the above figures, in conjunction with those given above, for the teaching of chemistry as a specific subject, we may say that in the public elementary schools of England and Wales there were during the last school-year about 10,000 scholars receiving instruction in chemistry, or about 1 in 364 in average attendance, or 1 in 450 on the total number of children on the register.

In the Appendix more detailed information is given as to the teaching of chemistry in one or two large towns.

Difficulties in the Way of Chemical Teaching in Public Elementary Schools. — Although a satisfactory course of instruction in chemistry might be based on the Code, it is seldom done. Children on leaving the infant schools pass into the standards where elementary science is only an optional subject. The first optional subject must be English, and if a second is taken it is usually geography, and in most schools—as, for example, in those of the Leeds district — there is practically no "elementary science" taught in the first four standards.

When children arrive at Standard V. they may take chemistry as a "specific" subject, but several difficulties are met with, of which the following are the chief:—

1. Between the infant school and the Fifth Standard there is generally a gap of four years, during which the faculties of observation have received no training, and the good beginning made in the infant school has not been followed up.
2. The expense and trouble of preparing experiments. This may, for example, lead to the teaching of physiology (by diagrams only) instead.
3. The smallness of the grant obtainable (4s. for a pass).

The third difficulty is partly overcome by school authorities making the teaching of chemistry as a specific subject preliminary to the classes held under South Kensington, the pupils of which obtain substantial grants; but a difficulty is experienced in co-ordinating the Code Schedule with the South Kensington syllabus, so that pupils on reaching Standard VI. may be only just ready for the South Kensington examinations in the following May. If a pupil is taught chemistry as a "specific" subject in Standard V. for one year, he is usually ready for the elementary stage South Kensington examination, but is not admissible for another year. (If the "Class" subject "elementary science" were taken in Standards I. to IV., as is so desirable, this difficulty would be further increased).

Most boys on reaching Standard VI. leave school, so that they do not take the South Kensington examinations, which is the only way for the school to earn the substantial grants which make science teaching "pay."

In consequence of these difficulties surrounding the teaching of chemistry as a "specific" subject under the Whitehall Department, the greater part of the chemical teaching in elementary schools is forced under the South Kensington Science and Art Department, and school boards are being led to establish higher grade schools, confined to boys who have passed the Sixth Standard and are able to prepare for the South Kensington examinations. They include those boys whose parents are of sufficiently good means to keep them at school after the age of fourteen. Such schools are regarded by many as going beyond the elementary education contemplated in the Education Act of 1870.

Conclusions. — Reviewing the foregoing statements, which I have endeavoured to keep free from merely personal opinions, I am led to the following conclusions:—

1. That the teaching of chemistry in public elementary schools is far from satisfactory in its organisation.
2. That the teaching of chemistry in public elementary schools from its earliest stages in the infant schools to its latest stages in higher grade schools should be under the control of one Educational Department only.
3. That if, as is admitted, the teaching chemistry, adopted at all, should be used as a part of general mental discipline, its organisation and control should not be separated from that of other branches of elementary education, that is to say, it should be conducted under the Whitehall Education Department.
4. That the present inspectorate is ill-adapted for the

* From a return kindly furnished by Major-General Donnelly, Secretary of the Science and Art Department.

supervision and control of chemical teaching, and that special or additional inspectors, suitably qualified, should be appointed.

5. That the Code regulations should be so amended as to give "elementary science" more chance of being adopted as a "class or optional" subject—*e.g.*, by incorporating geography and elementary science as one subject.

6. That the minimum qualifications for science teachers are too low, for, though it is possible for such teachers to inculcate facts, a high standard of scientific knowledge is absolutely necessary for the proper "educative" teaching of the most elementary chemistry.

7. That the peripatetic system is at present the only practicable way of obtaining sufficiently good chemical teaching.

8. That the science teaching in the Universities and University Colleges should be made available for the training of teachers of chemistry in public elementary schools.

9. That, as a rule, chemistry is presented to children in elementary schools in precisely the same way as to undergraduates in the Universities, and that this is the chief cause of unsatisfactory results.

10. That the routine schematic teaching of qualitative analysis which constitutes usually the "practical chemistry" of schools, though pleasing and interesting to the pupils, is most unsatisfactory and uneducative.

11. That there is urgent need of some book, or at least instructions, which shall show how chemistry may be approached naturally and logically from a study of common things and every-day phenomena.

12. That great latitude should be allowed to the teacher to work out a system of the kind indicated, suitable to the conditions under which he works.

13. That the teaching of chemistry as a specific subject cannot be expected to thrive in public elementary schools with only a 4s. grant as against the much larger sum obtainable from South Kensington, and that the Government grant should be awarded, not on individual written examination, but on oral examination combined with general supervision of the character of the teaching.

14. That true specialised technical or professional training in chemistry should not be attempted, but that it should begin not earlier than in recognised state-aided secondary schools, restricted to such scholars as have qualified themselves by a regular and satisfactory course in an elementary school.

Very exaggerated notions exist, and are becoming more and more prevalent, as to what may be properly attempted so far as the teaching of chemistry in elementary schools is concerned. The public do not realise that in the countries where science is most cherished and applied most extensively and successfully to industry (*e.g.*, Germany and Switzerland), the chemical and science teaching in the *elementary* schools is of the most simple and general character, and that the systematic teaching of science for technical purposes begins only in higher schools, polytechnics, and universities. This systematic teaching depends for its success no more on the previous training in science than on the previous training in arithmetic. It demands solely that the previous training shall not have given merely *information*, but that it shall have developed *intelligence*, that it shall have been rational and thorough, and have been administered by good teachers. In this country too much or too little is being attempted, and it is quite a common thing to find boys possessing a large amount of detailed "information" about chemistry, and a certain mechanical aptitude in chemical analysis, who are unable to do a sum in simple proportion or to write their own language correctly.

The most that can be properly aimed at in teaching chemistry in elementary schools is the training of the faculties of observation and of orderly thinking, and the stimulation of the instinct of inquiry, which is the possession of every "uneducated" child. By restricting the teaching to common things and occurrences this can easily be done, and so an interest aroused both in the phenomena of nature and in those involved in industrial operations. In this way there will be created an interest in and appreciation of chemistry amongst the many, and preparation made for the few who can proceed to the highest study of the subject, which alone is *directly* applicable to the advancement of industry.

(To be continued).

OBITUARY.

DR. JAMES PRESCOTT JOULE.

We deeply regret having to put on record the death of one of Britain's most illustrious physicists. Dr. James Prescott Joule died on October 11 in his seventy-second year. Though he wrote neither popular treatises nor separate works on the subjects of his studies, his researches and discoveries—especially that of the mechanical theory of heat—are of such capital moment as to be known to all students of chemistry and physics.

It will not be deemed irrelevant if we remind our readers that Joule never "went up" for any examination, and that throughout his life he worked not for rewards, or even honours, still less from emulation, but from the pure love of truth.

Dr. Joule was one of the surviving pupils of Dalton. He received the Royal Medal of the Royal Society in 1852 for having demonstrated the law of mechanical equivalence of work and heat, and in 1860 the Copley Medal of the Royal Society was adjudged to him, in connection with the same series of researches. In 1872 he was elected President of the British Association, but the state of his health debarred him from attending the meeting at Bradford. Since that time, though an invalid, he has quietly continued his researches.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—In a letter appearing in Chem. News, vol. lx., p. 184, "Cyclops" says that "it is in your columns *par excellence* that the real grit of an invention is to be ground out." This is a proposition with which I cordially agree, and, feeling convinced that your columns are always open for discussions tending to advance the ends of science, I request your kind insertion of the following explanations, which meet the comments of your correspondent:—

1. I use in the treatment of 1000 gallons of the sewage at Wimbledon about 6½ ozs. of herring brine. This quantity would contain* the equivalent of about 20 grains of propylamine—in the form of salts of the same. It is, however, not for the latter that I claim the disinfecting power, but for new gaseous reagent, resulting from the action thereon of the lime. This reagent I term "Aminol," and its effects have now been repeatedly and conclusively demonstrated. It is quite true that, to the minds of other than scientific men, the action of minute quantities of certain chemicals is startling, but (in the words of your correspondent) "the minds of chemists will not be so easily disturbed."

2. "Cyclops" says:—"It is passing through a second period of juvenility to be fighting the old lime fallacy; a ghost long since laid has raised its head, but this time

* *Vide* Girardin's analysis of herring brine.

cum grano salis." However admirable from a literary point of view this series of metaphors may be, "Cyclops" himself seems to have fallen into the "old lime fallacy," of which he speaks. Dr. Klein found experimentally that lime alone, in the same quantities as those employed in the "Amines" process, was incapable of sterilising. Winter-Blyth failed to sterilise with many times the quantity of lime I use, whilst Richard and Chantemesse in France, and Liborius on Pfuhl in Germany only succeeded in disinfecting by employing about twenty times my proportions. Cyclops evidently was not aware of these researches when he wrote his letter.

3. It is true, that a lime effluent would not be safe in a river; the "Amines" effluent, however, enters the river charged with a powerful disinfectant, which is only diluted *pari passu* with the dissolved organic matter.—I am, &c.,

HUGO WOLLHEIM.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
October 21, 1889.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

SIR,—Herr H. Wollheim, in his letter of October 9th, points out two errors in my report, which appeared in the CHEMICAL NEWS of September 27th (vol. lx., p. 157) and re-asserts a very serious mistake made in the circular or prospectus of the "Amines" Syndicate.

The quantities of lime herring-brine which I gave were doubtless incorrect, an error which I regret, but which involves no principle.

Mr. Winter-Blyth's researches are disposed of by the statement that the germicide agent is not trimethylamine, but "a new reagent evolved therefrom by the action of the lime." Would it be too much to ask Herr H. Wollheim, in the interests of science, to give the composition and properties of this reagent and to explain the *rationale* of its formation?

If Herr Wollheim and his friends think that all other sludges are a nuisance when *wet*, they have something yet to learn concerning sewage-treatment. There are other processes which not only claim but habitually do produce an inoffensive sludge alike when it contains 90 per cent of water as first drawn out of the tanks and at every subsequent stage. This I know from repeated personal observation, backed by the testimony of scores of independent witnesses. If Herr Wollheim had said we know of no other *lime* process he would have been right.—I am, &c.,

THE WRITER OF THE REPORT.*

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—In Spain, where the oldest mercury mines in Europe are situated, the general or common name of the red sulphide of mercury is "cinabrio," but in Castile it is called "bermellon." The "*b*" and "*v*" in Spanish are pronounced so nearly alike that only a well-educated Castilian makes or detects the difference. The "*ll*" has a particular sound in Spanish, which we have endeavoured to retain in the words "million" and "postilion," which are of Spanish origin.

English.	Spanish.
Million.	Millon.
Postilion.	Postillon.
Flotilla.	Flotilla.
Punctilio.	Puntillo.

The introduction of the "*i*" after the "*ll*" is an indication that an endeavour has been made to retain the foreign sound. "Postilion" and "punctilio" have lost one "*l*," but it is still heard in the "*i*"; whilst "flotilla" retains its Spanish orthography, but does not keep the sound of the two "*l*'s," and therefore does not take the "*i*."

The correct orthography of the word should be vermillion, which preserves both the origin and sound of its Castilian equivalent.—I am, &c.,

W. H. DARLING.

Manchester.

* CHEM. NEWS, vol. lx., p. 157.

CONSTANT WATER-BATH.

To the Editor of the Chemical News.

SIR,—I can testify to the efficiency of a constant water-bath similar to the one described by Dr. Davenport in the CHEMICAL NEWS (vol. lx., p. 178). A friend of mine, Mr. G. W. Slatter, A.R.C.Sc., &c., chemist at Saltaire, erected one eight years ago in his laboratory, the condensing arrangement being merely a thick lead pipe, eight yards long, running zigzag upwards, and being open at the top; this being, I think, a great advantage on Dr. Davenport's method.

Mr. Slatter recently informed me that he has only had to re-fill the bath once in eight years, and then only after repairs for leakage, although the bath has frequently been boiling day and night.—I am, &c.,

S. J. SPEAK, A.R.S.M.

Shipley, October 17, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 14, September 30, 1889.

The Application of High Temperatures to the Observation of the Spectrum of Hydrogen.—L. Thomas and Ch. Trépied.—The electric arc affords a certain and relatively easy means of rendering the hydrogen sufficiently luminous for spectroscopic observation, even with the use of great dispersions. On introducing the hydrogen between the carbons the authors observed immediately the appearance of the two lines Hα and Hβ. With a single prism Hα possesses a lustre comparable to that of the metallic rays; Hβ, blunted at its margins, recalled by its constitution the obscure ray, F, of the solar spectrum observed with a dispersion of about twenty prisms. With a dispersion equivalent to that of ten prisms Hα became much broader and blunted at its margins, presenting thus a certain analogy of the corresponding ray of the atmosphere, but still without presenting as marked a maximum; Hβ spread itself out considerably. Lastly, with the great spectroscope of Thollon (about 31 prisms of ordinary flint glass) Hβ is seen indistinctly.

The Connection of the Atomic Weights of Simple Bodies.—M. Delauney.—The author arrives at the conclusion that the atomic weights of the simple bodies are connected with each other by the addition of the square root of a whole number. This number is variable, but always harmonic, *i.e.*, containing no other primary factors than 1, 2, 3, and 5. The chain of atomic weights presents gaps, probably because we do not know all the simple bodies. We remark certain noteworthy places where the links of two bodies become ingrafted: these places correspond to atomic weights following each other in geometrical progression:—24Mg, 48Ti, 96Mo, and 192, probably an unknown body. The following is a specimen of the author's table:—

	Atomic Weight.	Additional Number.
H	1	
Li	7	$\sqrt{36}$
Be	9·25	$\sqrt{5}$
B	11	$\sqrt{3}$

Combinations of Copper Oxide with Amylaceous Bodies, Sugars, and Mannites. New Reagents for Proximate Analysis.—Ch. Er. Guignet.—The solution of cellulose in ammoniacal copper oxide is precipitated by the addition of a large quantity of water, and gives a very definite compound of cellulose and copper oxide, which does not retain ammonia when it has been well washed. If placed in contact with ammoniacal oxide of copper, starch, in its dry state, absorbs copper oxide very readily, so as completely to decolourise the solution. The action is still more rapid with starch slightly moistened. Starch-paste acts in the same manner, but more slowly. Pure water, and even ammoniacal water, only withdraws infinitesimal quantities of copper oxide from the compound. Under these conditions the starch combined with copper oxide is of a deep sky blue and retains ammonia. But if it is heated to 40° in presence of water it loses this ammonia, and becomes of a light green. At 80° the starch passes into the state of paste, retaining anhydrous copper oxide so intimately mixed that under the microscope each grain appeared covered with a blackish grey coating. By a very prolonged digestion with pure ammonia the starch combined with copper oxide is partially dissolved, the solution containing copper oxide and soluble starch. Inuline behaves in an analogous manner. Ammoniacal copper oxide does not throw down any saccharine matter, because the compounds formed by the sugars with copper oxide are very soluble in ammonia. It is not the same with ammoniacal copper (without excess of ammonia). This compound is readily obtained in the crystalline state by adding to ammonia very gradually copper sulphate pulverised and dried at 100°. The liquid heats strongly; it is raised to a boil for some minutes and let cool. Cane-sugar, milk-sugar (and probably the other isomers) do not precipitate ammoniacal copper sulphate. On the contrary, pure glucose (from honey), galactose, &c., precipitate the same reagent in a few moments. The reagent must not be used very concentrated or in excess, as it dissolves the precipitate. Inverted sugar obtained by the action of very weak sulphuric acid upon cane-sugar does not precipitate ammoniacal copper sulphate. It is the same with pure crystalline levulose derived from inuline. But if we add pure glucose to inverted sugar or to levulose the glucosic compound is deposited in a few hours, which seems to show that inverted sugar is a combination and not a mixture of glucose and levulose. Most bodies contained in the decoctions of vegetable matters do not precipitate ammoniacal copper sulphate. This reagent may, in many cases, be employed in preference to lead acetate, neutral or basic. The vegetable acids, the gums, and the pectic matters do not precipitate the ammoniacal copper salt.

Moniteur Scientifique, Quesneville.
Series 4, Vol. III., August, 1889.

The Periodic Law of the Chemical Elements.—M. D. Mendeleeff.—The "Faraday Lecture."

The Life and Researches of Dmitri Ivanowitch Mendeleeff.—An article founded on Prof. T. E. Thorpe's paper in *Nature*.

Industrial Review.—A selection of patents relating to the chemical arts.

Ochres, Sienna Earths, and Umbers.—G. Hurst.—From the CHEM. NEWS.

Aluminium.—Sir H. Roscoe.—From the CHEMICAL NEWS.

The Sophistications of the Vegetable Oils of Commerce: a Critical Examination of the Qualitative and Quantitative Methods for their Analysis.—P. J. S. Girard.—The introduction to a very voluminous paper.

A New Process for Mordanting with Chrome.—G. Saget.—If we pour a solution of potassium bichromate into calcium hydrosulphite with an excess of lime, chromium oxide is at once precipitated. Cloth padded in bichromate and steeped in calcium hydrosulphite becomes green, and attracts all colouring-matters which dye chromium oxide. At 40° the action is immediate.

Industrial Society of Mulhouse.—Session of the Chemical Committee, June 12, 1889.—The Secretary read a paper by M. G. Galland on dyeing with indigo and indophenol in a mixed vat according to the process of Durand and Huguenin. M. A. Schlumberger gave an account of the date when "ungreenable" blacks were first produced at the Mer-Rouge Print works.

Action of Ammonium upon Metallic Magnesium.—H. N. Warren.—From the CHEM. NEWS.

The Rapid and Certain Detection of Antimony in Minerals.—A. Johnstone.—From the CHEM. NEWS.

Physical Properties of the Graphite obtained from Different Metals after its Elimination by Dilute Acids.—H. N. Warren.—From the CHEM. NEWS.

Decomposition of Nickel and Cobalt.—From the CHEM. NEWS.

Lixiviation of Silver Ores with Solutions of Hyposulphite and Special Relation with the Russell Process.—Dr. Stettefeldt.—From the CHEM. NEWS.

On Potassium Chlorate.—Dr. Hodgkinson and F. Lowndes.—From the CHEM. NEWS.

Journal de Pharmacie et de Chimie.
Series 5, Vol. XX., No. 3.

Origin of the Artesian Waters of the French Sahara.—M. Jahacle.—These waters are not as some suppose in filtrations from an interoceanic current, from which they differ in composition, especially by the excess of calcium sulphide, the relatively smaller quantity of chlorides, and the abundant presence of nitrates. They are derived from atmospheric water which takes up salts in filtering through the soil and the rocks.

The Gum of Australia.—Ch. Naudin.—We note in this paper the interesting suggestion to induce in acacias the gummy diathesis by grafting or by inoculation.

Safranine as a New Reagent for Glucose.—The author dissolves 10 centigrms. safranine in 100 grms. water, pours 2 to 3 c.c. of this solution, adds a few drops of the supposed glucosic solution, then 2 to 3 c.c. of soda-lye at 10 per cent, and heats in the water-bath. Between 60° and 65° the safranine is reduced, forming a colourless compound, insoluble in the cold, which gives a milky precipitate. The oxygen of the air regenerates the safranine, forming a red colour on the surface of the liquid.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. IV., Nos. 42 and 43.

These numbers contains no chemical papers.

No. 44.

Report Delivered by M. E. P. Berard, on behalf of the Committee of Chemical Arts, on a Furnace for the Manufacture of Coal-gas, Presented by M. André Coze.—The peculiarities of this furnace cannot be described intelligibly without the accompanying figures.

Journal fur Praktische Chemie.
Vol. xl., Parts 1 and 2.

Derivatives of Meta-toluquinazolin and of Meta-homo-anthranilic Acid.—Stefan von Niementowski.—The author investigates orthonitroparatolunitrile, the corresponding amido-compound, orthoacetamidoparatolunitrile, orthoazoxyparatolunitrile, orthoamidoparatoluylamide, δ-oxymetatoluquinazoline, β-methyl-δ-oxymetatoluquinazoline, toluylazimide, metahomoanthranilic acid, orthoformamidoparatoluylic acid, orthoacetamidoparatoluylic acid, metamethylorthouramidobenzoyl, nitroorthoacetamidoparatoluylic acid, and nitroorthoamidoparatoluylic acid.

Remarks on the Treatise by J. Wislicenus, "On the Geometrical Constitution of the Crotonic Acids and their Halogen Substitution-products.—Arthur Michael.—A controversial paper, not susceptible of useful abridgment.

Fluorine Compounds of Vanadium and of its Nearest Analogues.—Emil Petersen.—There is a very decided analogy between the fluorine compounds of vanadium sesquioxide and of chromium oxide in crystalline form, method of preparation, solubilities, behaviour when heated, and in colour. This shows that vanadium sesquioxide must be placed in the group of analogous basic oxides; those of chromium, iron, manganese, and aluminium. Titanium sesquioxide seems also analogous to this group.

Alloisomerism in the Cinnamic Acid Series.—Arthur Michael and Hunter Pendleton (Third Communication).—According to the experiments of the authors the isomeric relations of the chlorocinnamic acids are quite analogous to those of the corresponding bromocinnamic acids, and the known facts can be understood without assuming a change of position of the halogen.

On the Constitution of Benzol.—Ad. Claus.—A controversial paper. The author points out certain questionable matter in A. Baeyer's second memoir on the reduction of the hydroterephthalic acids. In this memoir Baeyer draws inferences on the constitution of benzol in direct opposition to the conclusions arrived at in his first memoir. Above all he seeks to rehabilitate Kekulé's formula for benzol which he had previously shown to be untenable.

Calorimetric Researches.—F. Stohmann.—In this seventeenth memoir the author, in conjunction with Kleber and Langbein, examines the combustion-heat of benzol and other hydrocarbons. He confirms the accuracy of the thermic value of benzol as already determined. In the solid homologues of benzol the combustion-heat rises by 155·1 cals. on the introduction of each methyl group. If benzol passes into diphenyl owing to the substitution of an atom of hydrogen by a phenyl-group the thermic value rises by 717·0 cals. If in the hydrogen molecule an atom of hydrogen is replaced by phenyl, the combustion-heat of the benzol vapour thus arising is higher than that of the hydrogen molecule by 718·5 cals. The formation of diphenyl from benzol by abscission of two atoms of hydrogen takes place without perceptible evolution of heat. The combustion- and formation-heats of anthracene and phenanthrene are not different. On the conversion of benzol into naphthaline, the combustion-heat increases each time by about 458 cals.

The Action of Hydriodic Acid upon the Crotonic Acids.—Arthur Michael and Paul Freer.—On exactly repeating the experiments of Hemilian the authors obtained not a trace of a liquid addition-product.

NOTES AND QUERIES.

Fluor-spar in Zinc Blende.—Will any of your readers be good enough to let me know—(1) If the presence of fluor-spar in zinc blende has any injurious effect upon the working of the latter. (2) What would be the effect? (3) What would be the remedy?—SPAR.

MEETINGS FOR THE WEEK.

FRIDAY, Nov. 1st.—Physical, 5. "On Electrifications due to the Contact of Gases with Liquids," by J. Enright. "On a New Electric Radiation Meter," by W. G. Gregory, M.A. "On a Physical Basis for the Theory of Errors," by C. V. Burton, D.Sc

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DESTRUCTIVE DISTILLATION: A Manualette of the Paraffin, Coal-Tar, Rosin Oil, Petroleum, and Kindred Industries. With Illustrations of Shale Retorts. 8vo., 4s.

WATER SUPPLY AND SEWAGE: Short Notes for Non-Technical Readers. 8vo. 1s.
London: GURNEY and JACKSON.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that CHARLES FREDERICK HENGST, of 20, Burwash Road, Plumstead, County Kent, has applied for leave to amend the Specification filed in pursuance of the application for Letters Patent No. 13650 of 1888, for "An improved smokeless safety gunpowder."
Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 16th October, 1889.
Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.
(Signed),
H. READER LACK,
Comptroller-General.

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THE CHEMICAL NEWS.

Vol. LX. No. 1562.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

Although aluminium is one of the most widely distributed of the elements, entering into the composition of nearly two hundred minerals, its oxide, alumina, was regarded as identical with lime until, in 1754, Margraff proved it to be a distinct substance.

In 1807, Davy, so successful with the oxides of the metals of the alkalies and alkaline earths, attempted to decompose alumina by the battery, but failed; and it was not until the year 1828 that Wöhler, by heating the chloride with metallic potassium, first obtained aluminium as a grey lustrous metallic powder, and eighteen years later in globules not larger than pin-heads. From these, with extreme ingenuity, he determined the principal properties of the metal. In 1854, Deville (at that time Professor of Chemistry in the Ecole Normale, Paris), in course of some researches on the chloride, obtained a button of pure aluminium by the decomposition of the chloride with sodium, and on the 4th February in that year read a paper, describing his discovery, before the Academy of Science. As a result, a committee was formed to carry on experiments, 2000 f. being granted to meet expenses. On August 14th, he read a second paper before the Academy, exhibiting several bars of aluminium, and caused a medal of the metal to be struck and presented to the Emperor.

In March of the next year, experiments on a large scale, at the Imperial cost, were instituted at Javel; and on June 18th, Deville presented to the Academy, through M. Dumas, large bars of pure aluminium. These experiments are said to have cost the Emperor 35,000 f. (£1458).

Deville's method, modified in details, is still the chief of the chemical methods of preparing aluminium on a commercial scale, and is dependent on the cost of the metallic sodium and the double chloride of aluminium and sodium, which is the compound used in the most important of the present day processes.

Pure aluminium is a highly lustrous metal, white with a faint tinge of blue in colour. It resists the action of air and moisture, even at high temperatures; is not blackened by exposure to the action of sulphuretted hydrogen or the alkaline sulphides; and is not attacked by fused nitre, nitric, or dilute sulphuric acid. It dissolves readily in hydrochloric acid, or in solutions of the alkalies.

Its density is but two and one-half times that of water. Compared with other metals its density is as follows:—

Metal	Density.	Compared with aluminium.
Platinum	21·5	8·6
Gold	19·3	7·7
Lead	11·4	4·8
Silver	10·5	4·2
Copper	8·9	3·6
Iron	7·8	2·9
Tin	7·3	2·8
Zinc	7·1	2·8
Aluminium..	2·5	1·0

In a paper read by Mr. W. H. Barlow before the British Association, 1882, its tenacity is given at twelve tons to the square inch: but weight for weight, it would equal high class steel, or 36 tons per square inch. Its elasticity is almost equal to that of silver. Is ductile, can be drawn into very fine wire, and is almost as malleable as gold. Its thermal conductivity is about two-thirds that of copper; its electrical is given by Deville as eight times that of iron. Its specific heat is 0·22; it melts at 1300° F., but exhibits no tendency to volatilise, even though heated in a carbon crucible in a blast-furnace to high temperatures.

The extreme lightness of aluminium, its power of resisting the action of air, moisture, and sulphuretted hydrogen, give it an advantage over silver, which it equals in tenacity and elasticity, as a material for jewellery and for scientific and astronomical instruments.

The greatest value of aluminium is, as yet, in its alloys, and it is with their production in the electric furnace I propose to deal to-day; and I may remark that the successful application of the intense heat of the electric arc to the production of metals on a commercial scale, marks a new departure in electro-metallurgy, of which we cannot over-estimate the importance, rendering it possible to produce rich alloys of aluminium at half the cost of any other process, and so widening the field of their application to an extent hitherto unknown.

Messrs. Cowles' first experiment was with a very refractory zinc ore, containing silver, which they had failed to reduce in an ordinary furnace. A fireclay tube was taken, filled with a mixture of the crushed ore and charcoal powder, a bundle of electric light carbons inserted in each end, and a current from a small dynamo sent through the mass. In a short time the ore was reduced, but the fireclay tube was partly melted, showing the necessity for a lining that would protect the furnace walls from the intense heat. Powdered charcoal, a very feeble conductor of heat and electricity, was tried, but it was found that after a time it became converted into graphite, thus becoming a conductor; as the smelting proceeded, changing gradually from the inside to the outside, and, as the hot zone expanded, causing loss of energy, and eventually destroying the furnace. Mr. Alfred H. Cowles then suggested soaking the charcoal powder in milk of lime and drying before use—this proved successful, each particle of charcoal being coated with a film of lime which insulates it and prevents electrical conduction between neighbouring particles even after the charcoal is converted into graphite. Messrs. Cowles now found that they had a furnace that would enable them to conduct metallurgical operations at a temperature hitherto unknown outside the laboratory; and after some experiments with corundum, they, acting in conjunction with Professor Mabery, set up the first plant for the production of aluminium bronze, ferro-aluminium, and silicon bronze, at the works of the Brush Electric Co., Cleveland, Ohio, U.S.A. On the 20th of January, 1886, Mr. E. H. Cowles read a paper before the Franklin Institute, describing the electric furnace and a process of making aluminium bronze. The Institute thought so highly of the importance of the discovery that they awarded to Messrs. Cowles the "Elliot" gold medal, the highest honour in the gift of the Institute. The City of Philadelphia awarded them the "John Scott legacy" medal, this being the only instance of the two awards falling to the same inventors.

In 1887, Mr. E. H. Cowles was elected a Fellow of the Royal Society.

The results obtained at Cleveland were so satisfactory, though using only a dynamo of 300 Ampères with E.M.F. of 60 volts., that in 1886 the Cowles Co. commenced the works at Lockport, N.Y., U.S.A. The works at Lockport commenced operations with a Brush dynamo giving a current of 1600 Ampères, with an E.M.F. of 45—50 volts; to this has been added two dynamos each capable of supplying a current of 3000 to 3200 Ampères, with an

* Read before the British Association, Section B, Newcastle Meeting.

E.M.F. of 55 to 60 volts. A fourth dynamo is now building of 3000 Ampères. One striking feature of the Lockport works is the use of water-power, the dynamos being actuated by two powerful turbines, 30 inch diam. = 500 h.p.

The number of furnaces in operation are 14, producing about 300 lbs. of aluminium contained in alloys per 24 hours. Four additional furnaces are now building. I will now describe the English works of the Company at Milton, Staffordshire.

These, the first electro-metallurgical works established in Europe, are situated near Milton station, on the North Staffordshire Railway, with which system they are connected by a siding, and also abut on a branch of the Trent and Mersey canal—thus affording facilities for cheap transit of raw material, coal, and finished products.

The experience at the Lockport works showed conclusively that great economies were to be expected from increasing the size of the furnaces and the strength of the electric currents; but no current of more than 3000 Ampères had been used up to the time the Milton works were planned.

Mr. Cowles then prepared a specification for a dynamo to give a current of 5000 Ampères at 60 volts., and eventually Messrs. Crompton's designs were accepted. This dynamo is of 500 h.p., and furnishes a current of 5000 to 6000 Ampères, with an E.M.F. of 50 to 60 volts. It is said to be the largest machine (at least in regard to quantity of current) in England, and probably in the world. I will not describe this magnificent machine more fully, as it was the subject of a very interesting paper read by Mr. Crompton before the G section of the Association last year.

The boilers supplying steam to the works are of the Babcock-Wilcox type, representing 600 h.p., and are fitted with mechanical stokers; by this means one man can easily attend to the generation of steam for the whole works.

The main engine, used for driving the dynamo only, is a compound condensing horizontal tandem engine, made by Messrs. Pollitt and Wigzell, of Sowerby Bridge, and is well worth noting for its beautiful workmanship. Its motion is, indeed, so silent, that, with your back to it at the moment of starting, you cannot tell whether it is in motion or not. It is of 600 h.p., and is provided with automatic expansion gear; and the centrifugal governor maintains the speed at 76 revolutions. It is needless to say that work of this kind involves rapid fluctuations of load, and as an additional precaution against racing, the engine is fitted with Tate's electrical stop-valve, which stops the engine automatically if the speed exceeds a certain limit. It can also be stopped from various points in the engine and furnace rooms by means of push-buttons connected in parallel with the main circuit leading to the Tate's valve.

The engine has a 23-inch high pressure and a 43-inch low pressure cylinder, the stroke is 5 ft., the average steam pressure being 85 lbs. The fly-wheel is 20 ft. in diameter and weighs 20 tons; it is geared to the dynamo by 18 driving ropes, so that the dynamo makes 5 revolution for each revolution of the engine.

From the dynamo the current is led by copper bars to an enormous "cut-out," calculated to fuse at 8000 Ampères. This is probably the largest ever designed, and consists of a framework carrying 12 lead plates, each 3½ inches broad by $\frac{1}{10}$ inch thick. From this it passes into the furnace rooms; a current indicator is inserted in the circuit, consisting of a solenoid of 9 turns (this was cut out of a cylinder of cast-copper by means of a parting tool, in a screw-cutting lathe). In the solenoid is an iron core suspended by a spring; the movement of this is communicated to two pointers, one dial being placed in the engine-room, the other in the furnace-room. The range of the indicator is such that the entire circle of 360° = 8000 Ampères.

There are two furnace-rooms, each containing 6 furnaces; the first room contains the bronze furnaces, in which is carried on the manufacture of aluminium-copper and silicon-copper; the second is devoted to the production of ferro-aluminium.

The furnaces are rectangular in form, built of fire-brick, the internal dimensions being 60 inches × 20 inches × 36 inches; into each end is built a cast-iron tube through which the carbon electrodes enter the furnace. Each electrode consists of a bundle of 9 carbons, each 2½ inches diameter, attached to a head of cast-iron, for ferro-aluminium, or cast-copper when cupro-aluminium is made. Each carbon rod weighs 20 lbs.

Quite recently it has been possible to obtain carbons 3 inches in diameter, weighing 36 lbs.; these are employed in bundles of 5.

The "head" of the electrode is secured to the copper rods or "leads," which can be readily connected with or disconnected from the flexible cables supplying the current.

Each cable is secured to slides running on omnibus bars of copper overhead, so that it can be brought into position opposite the furnace to be used.

The electrodes are arranged so that it is possible, by means of a handle and screw, to advance or withdraw them from each other in the furnace.

Lining the furnace is the first operation preparatory to smelting. This is done by covering the bottom of the trough with a layer of prepared charcoal.

Oak charcoal is used. This is ground under edge runners, treated with milk of lime, and dried, first in a steam-jacketted revolving drum, and afterwards on a hot iron plate. Each particle of charcoal is thus coated with an insulating film of lime.

The electrodes are now arranged in the furnace, and a "former," consisting of two pieces of sheet-iron connected by stirrups, arched so as to fit over the electrodes, forming a box without top or bottom (the size being dependent on the charge used), is dropped over the electrodes. Prepared charcoal is rammed into the space between the iron sheet and the firebrick walls of the furnace. This done, the charge of ore, mixed with coarse charcoal, and the metal to be alloyed with the aluminium, in form of turnings or granules, is placed inside the iron box, after which this is carefully withdrawn. Some broken pieces of carbon are arranged so as to connect the electrodes and start the current. The charge is then covered with coarse charcoal, and the cast-iron cover, having a hole in the centre for the escape of gases, is lifted into place, and luted so as to prevent the entrance of air.

The commencing current is about 3000 Ampères, gradually increasing to 5000 Ampères in the first half hour. The time occupied by a "run" is about one and a half hours. Soon after starting, the gases escaping from the orifice in the cover take fire and burn with a white flame; this gas consists mainly of carbonic oxide, with small quantities of the hydrocarbons and nitrogen. On the conclusion of the run the furnace is allowed to cool, the melted alloy collecting in the bottom of the furnace; the next furnace ready charged is connected, so that the process is a continuous one, the furnaces being successively charged and connected. A form of furnace in which the metal is tapped from the bottom has given very satisfactory results.

The energy required to produce 1 lb. of contained aluminium depends, of course, upon the grade of alloy, the average being 18 h.p. per hour.

The crude metal from the furnace is then refined and re-melted in a reverberatory furnace; each "run" is sampled, and the percentage of aluminium ascertained by analysis.

The nature of the reaction that takes place in the electric furnace is not very easy to ascertain. The reduction of the ore takes place in an air-tight box, and in presence of an enormous excess of carbon. It may be

assumed that, at the intense heat of the electric arc, the ore melts and gives up its oxygen to the carbon,—

$$Al_2O_3+3C=3CO+Al_2.$$

The presence of copper or iron is immaterial, as the reaction takes place with ore alone; but in absence of the alloying metal the liberated aluminium absorbs carbon and is converted into a carbide.

Prof. Hampe, however, contends that the reaction is in two stages, the first being electrothermic, in which the ore melts; the second electrolytic, in which electrolysis of the molten oxide takes place, aluminium being liberated. Supposing an alternating current is used in the furnace instead of the continuous, and that we have a high number of alternations, from recent experiments with alternating currents we know that very slight, or no electrolytic action occurs; if then we get equal results, it would go to prove that the action is thermic and *not* electrolytic.

An experiment was made by the Cowles Co., using an alternating current.

The furnace used was 48 inches × 12 inches × 24 inches, with current of 900 Ampères with E.M.F. of 50 volts. Alternations per minute, 11,000.

At the end of one and a half hours we obtained 45 lbs. of 4 per cent aluminium bronze.

This investigation was purely of an experimental character, and it cannot be doubted that on the larger commercial scale the result would be more satisfactory.

The results obtained were identical with those given by the continuous current in every way, the resultant slags similar in composition.

The slag from the electric furnace is really only melted unreduced ore, and not a slag in the proper sense of the word. Its approximate composition is:—Al_2O_3, 90; SiO_2, 2·00; Fe_2O_3, 4·00; CaO, 3·9; P, 0·10.

The charcoal from the whole linings, which has been partially converted into graphite, is re-crushed and treated with milk of lime, dried as before, and thus used many times over. The crude metals from the "runs" is re-melted with fluor-spar as a flux, and tapped from the reverberatory furnace into ingots or plates. The refinery slag is put into a revolving drum for breaking into pieces, and then washed to remove carbon — the entangled particles of alloy are thus recovered and are worked up with other charges. These operations are carried out in a separate building—the "reclaiming house."

These works produce about 200 lbs. of contained aluminium per twenty-four hours; the most valuable alloy being aluminium-bronze, which is supplied in grades containing 1¼ to 11 per cent aluminium. To obtain these the rich furnace product containing 15 to 20 per cent aluminium is re-melted and reduced to the desired percentage with metallic copper, and cast in 12 lb. ingots.

(To be continued).

MILK ANALYSIS.

By Dr. BENNETT F. DAVENPORT.

In the discussion of the relative merits of the different methods of milk analysis, which was published in a recent number of the *Analyst*, the many advantages of a simple modification of Wanklyn's method does not, I think, receive its due consideration. This modification, which I have adopted, I have already published in my Annual Report as Milk Inspector for the City of Boston, Mass., 1885, and as analyst to the Massachusetts State Board of Health in their Annual Report for 1886, p. 138. As being now the method generally followed by most of the official milk analysts in New England, a simple description of it may be of interest to others.

The 5 grms. of milk are weighed off in a large flat-bottom platinum capsule of full 2½ inches diameter on the bottom, and about 3 inches across the top. The ½-inch high side turns up from the bottom, not with a sharp angle, but slight rounding, this being about the curve with which the milk runs up the rim of the capsule drawn by capillarity. The milk, in drying down, does not thus form any thicker deposit at the angle of the side than elsewhere upon the about 5 square inches of bottom surface of the capsule. This relatively large amount of surface, one square inch to each grm. of sample taken, causes each inch to be covered with only a little over a single grain of dried milk solids. The deposit is therefore so very thin as to be readily exhausted of its fat in its subsequent treatment with boiling petroleum naphtha. When using such small dishes as were originally proposed by Wanklyn the residue would be so thick, that is about three times, as would naturally render any such rapid method of extraction as I employ impossible, as the English analysts have learned. Each capsule has its serial number engraved upon it, and they are made to weigh a little over 25 grms. each, that the bottoms may be stiff enough to remain perfectly flat, a matter of very great importance. They are also made to differ from each other only in the second and third places of decimals, so that only those weights have to be changed in many weighings, which is a matter of no little saving of labour where many score of weighings are to be made each day. A table of their weights is kept within the case of the scales. These capsules containing their samples are placed upon a constant-level closed-top water-bath of the peculiar construction described in the *Journal of Analytical Chemistry*, Vol. iii., Part 3, p. 269. This will hold 25 capsules at a time. Here, being surrounded by an atmosphere not already nearly saturated with moisture, as would be the case if they were upon a water-bath with openings on its top, they quickly evaporate to apparent dryness. They are then transferred for their final drying to a constant weight to one of Weisnegg's large porcelain-lined air-baths, regulated to the constant temperature of 105° C. Here they are dried in about half an hour, when they are cooled in a desiccator and each weighed immediately upon being taken out to guard against their rapid gain in weight from exposure to the air. Replaced upon the closed-top water-bath, the capsule is filled from a wash-bottle with petroleum naphtha of the quality of the benzine of the "U.S. Pharmacopæia," revision of 1880. This, unlike ether, will dissolve out neither milk-sugar nor lactic acid from the dried milk-solid residue. Moreover, one gallon of it costs but as much as one pint of ether would, which is a matter of some little consequence to one like me, who has had to use about 100 gallons of it in milk analyses during the past five years.

The naphtha in the capsule, after being allowed to boil down about one-half, is decanted off against a rod into a basin to guard against the remote possibility of some flakes of milk residue being poured off with it. Replaced upon the bath, the capsule is refilled with naphtha. This boiling up and decanting off is repeated three to four times, when, after the last one, the outside of the capsule is washed off with naphtha played upon it from the wash-bottle to prevent any residue of fat being left there. The capsule then finally replaced upon the bath to dry off the naphtha, is then cooled and weighed as before, the butter being rather determined from the loss of weight in the solids than by the weight of the evaporated washings.

The ash is made by ignition of the capsule over a one-inch wide Bunsen lamp, which thus gives so wide a flame as not to require a heating to a high temperature at one point, and thus a possible loss by the volatilisation of the potassium chloride. The milk-sugar I determine by the use of a Soleil-Ventzke saccharimeter in the same manner as has now been several times described in the journals by Drs. Wiley, Vieth and others. The other ingredients which reduce copper in Fehling's solution, are not thus reckoned as sugar, by which the apparent

amount of albumenoids present, which are obtained by difference, would be diminished.

The peculiarities of my modification is, then, the use of an evaporating capsule of such a very large relative area as will leave the residue thin enough to be readily exhausted by the boiling naphtha. Thus, a diameter of 2½ inches in the capsule will do for 5 grms. of better than average quality of milk, with a surety that there will not be as much as one-tenth of one per cent of fat left as a maximum error. And surely this is fine enough for all commercial work, and it is much to be doubted if much which affects to be more accurate by a decimal than this is really so. The method, as involving no transfer of substance, cannot well be made more simple for the determination of total solids, fat, and ash. When the average life of such an evaporating capsule under reasonable usage is considered, it cannot well be cheapened, although the outlay for a kilo. of platinum for 40 capsules like mine does, it is true, involve an original expense of nearly 400 dollars. The shape of my capsules makes possible completeness of extraction with the solvent used, and the construction of the closed water-bath hastens the process in no small degree.—*Journal of Analytical Chemistry*, Vol. iii., Part 3, July, 1889.

RAPID ESTIMATION OF FAT IN MILK.

By A. W. STOKES, F.C.S., F.I.C. (Public Analyst).

IT has become very much the custom of late with those who have to analyse large numbers of milk samples to determine only the total solids and the specific gravity. From these the fat can be calculated with great accuracy, thanks to the very excellent formulæ of Messrs. Behrend, Morgen, Fleischmann, Clausnitzer, Mayer, Hehner and Richmond. In cases, however, where the milk has become sour, or where preservatives have been added, this calculation is either impossible or misleading. Other cases arise where the results of the calculation do not agree with one's experience of the relative proportions of the sample's constituents. In such cases it is usually necessary to resort, for exact determination of fat, to the Soxhlet, Adam's paper coil, or the plaster-of-paris method. All these need many hours for a single determination, as well as special apparatus and attention.

In the CHEMICAL NEWS, vol. lviii., p. 197, was the following full translation of an abstract from the *Zeitschrift fur Analytische Chemie*, Vol. xxvii., Part 4 :—

"Dr. Werner Schmid takes a test-tube of about 50 c.c. capacity, graduated in tenths of a c.c., introduces 5 c.c. of cream or 10 c.c. of milk, accurately measured, adds 10 c.c. of strong hydrochloric acid, boils, with shaking, until the liquid turns dark brown, cools by placing the tube in cold water, adds 30 c.c. of ether, shakes round, lets stand, measures the volume of the ethereal solution, draws off 10 c.c. with a pipette, evaporates down in a weighed porcelain capsule on the water-bath, and finally in an air-bath at 100°. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been rightly conducted the ether separates from the aqueous solution clear, without the slightest turbidity. The ethereal solution, as it flows out of the pipette, should not show any watery drops. The results are perfectly accurate, and differ from each other and from the ordinary gravimetric methods by less than one-tenth per cent. The operation requires at most fifteen minutes."

Neither in the original nor elsewhere could I find any further particular, or any evidence of the working of this method. I have now for just one year tried this method on some hundreds of samples of milk, both in competition with other methods and against the calculated results obtained from sp. gr. and total solids. For this last I have used the admirable table of calculations of Messrs. Hehner and Richmond in the *Analyst*, vol. xiii., p. 26.

In a paper contributed to the *Analyst* of Feb., 1889, I showed the comparative results of this method and some others; but as the method of working there described is not the best, the results there recorded are not by any means as close as they should be. The method now adopted is as follows :—

Into special tubes (to be obtained of Messrs. Townson and Mercer), which are partly graduated up to 50 c.c., pipette 10 c.c. of the milk, if fresh, and then pour direct from its bottle some HCl roughly to the 20 c.c. mark. If the milk is a sour sample, weigh out 10 grms., and, with a small wash-bottle containing strong HCl, wash the milk into the tube till it is full to the 20 c.c. mark about. Now boil the mixture with frequent shaking till it turns brown. Merely heating it to the boiling point of water by immersion in a water-bath is not sufficient. Leave for about three minutes to stand; the colour will darken considerably, while thus standing, without further heat. Cool by immersion in water; fill up roughly to about the 50 c.c. mark with ether. It is not necessary that the ether should have been previously washed with water unless it contains more than 3 per cent of alcohol. Cork the tube and shake the mixture for half a minute; let settle for five minutes. Accurately pipette off 20 c.c. of the supernatant ethereal solution into a tared dish, evaporate off the ether, dry in air-bath, and weigh the residual fat. It is advisable to take at least 20 c.c. of the ethereal solution, so as to avoid the errors of high multiplication. It is perfectly easy to pipette off accurately 20 c.c. of the ethereal solution; the presence of fat in the ether prevents the difficulty that is found in pipetting off ordinary ether. Now notice how many c.c. of ethereal solution are left in the tube. Here there is sometimes a slight difficulty, since above the sharp line that separates the brown mixture of HCl and milk from the colourless ethereal solution sometimes there floats a fluffy narrow stratum of casein. If, however, three quarters of this stratum be assumed to be ether a correct reading will be made. From the whole quantity of ethereal solution originally present the percentage of fat in the milk is now calculated.

The whole process, doing at the same time a number of samples, need not take more than twenty minutes. Its accuracy is not excelled by any other process; the process is simple; the reagents are those found in every laboratory; almost all the ether and the HCl can be recovered if thought worth while; the only special apparatus needed is a cheap calibrated test-tube.

The HCl and the milk in the process should not be boiled together more than two minutes, else the ether will take up a caramel-like substance. Very highly watered milks do not turn a dark brown because of the small amount of milk-sugar present; while condensed and sugared milks become almost black.

An example may show the calculation required.

10 c.c. of a milk having the sp. gr. 1031 and giving 12 per cent by weight of total solids, when treated thus, gave, in 20 c.c. of ethereal solution, 0·277 grm. of fat. There were left in the tube 6·5 c.c. of ethereal solution, making a total of 26·5 c.c. Then—

$$\frac{0{\cdot}277 \times 26{\cdot}5}{2}$$

=3·67 per cent in 100 c.c. of the milk. Dividing this by the sp. gr., 1031, we get 3·55 per cent by weight of fat in the sample. Calculating from the sp. gr. and total solids, the fat should be 3·54 per cent.

To show the average results obtained I give the results on 12 samples of milk. These are not selected in any way except to show how the method answers both with rich and poor milks (see Table, next page).

These are not made-up milks, but those received in the ordinary way from various parishes under the Adulteration Act. The difference, with ordinary care in working, between the observed fat and the calculated fat never comes to the first decimal point in the percentage.

Sample.	Total solids.	Fat found.	Fat calculated.
No. 1 ..	15·64	6·54	6·57
„ 2 ..	13·60	5·16	5·14
„ 3 ..	11·68	3·81	3·82
„ 4 ..	11·46	3·50	3·52
„ 5 ..	11·40	3·26	3·25
„ 6 ..	11·40	3·25	3·25
„ 7 ..	11·30	3·14	3·16
„ 8 ..	9·86	2·87	2·88
„ 9 ..	11·30	2 60	2·60
„ 10 ..	10·20	1·94	1·97
„ 11 ..	8·90	1·86	1·85
„ 12 ..	9·61	1·33	1·32

Like most processes, it requires a little experience before exact results are attained. But the personal equation does not influence the method, for some of the many samples were done by my assistant, Mr. E. Michael (to whom I owe many thanks for care shown), and then repeated by myself, with the same results. In many cases part of the operation was done by one and the rest by the other; results came out just the same in agreement with the calculated fat. To ensure accuracy for the calculated at the total solids were dried over the water-bath and then in the air-bath, using flat-bottomed or glass dishes of 2½ inches diameter, and always taking about 5 grms. of the milk.* The sp. gr. was very carefully taken at 60° F. either by the Westphal balance or by the sp. gr. bottle.

In milk the fat is undoubtedly in some way held by the casein; in this process the strong boiling HCl destroys the casein and liberates the fat; the ether afterwards dissolves the fat. This ethereal solution is always slightly acid, but on evaporating off the ether the acid is also got rid of and only pure fat remains. Analysis of several samples of this fat shows it to be free from any other of the milk constituents. I am doubtful if any fat at all remains in the mixture of milk and HCl. If there be any, it must be exceedingly minute in quantity, and cannot influence the results.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Concluded from p. 203).

Appendix.

1. *Remarks on Finkener's Method of Direct Weighing of the Phosphomolybdate.*

As compared with that of Hehner, the method proposed by Finkener for the direct weighing of phosphomolybdate deserves the preference, since it avoids the following defects, which are inherent in the process of the former chemist. It dispenses with the hazardous washing of the precipitate with water (or with alcohol at 45 per cent), the tedious and repeated evaporations of the ammoniacal solution, and the troublesome drying of the residue, which is very sensitive to any elevation of temperature. Hence it is at once more trustworthy and more expeditious. The objection raised by Hehner, that the phosphomolybdate is easily reduced on drying, may be set aside if the following precaution is used:—The precipitate, after washing with a 5 per cent solution of ammonium nitrate, slightly acidulated, is dissolved in warm dilute ammonia. If the precipitate, as it is done by Finkener, is washed off the filter, the solution, as it contains fibres of paper, must not be evaporated until it has been filtered once more. The filtrate is received in the capsule and evaporated along with the washings until the liquid retains only a faint odour of ammonia, dilute nitric acid is added for the complete precipitation of the phosphomolybdate, and again evaporated as Finkener directs. The thick residue is heated over a wire gauze, at first gently and afterwards, when it ceases to froth, more strongly, until the ammonium nitrate is entirely expelled. The temperature of the crucible may reach 160°—180°. When a watch-glass, placed over the crucible, does not become coated after half a minutes' exposure, all the nitrate is volatilised. The yellow pulverulent residue is triammonium phosphomolybdate, free from moisture and acid, and after drying in the desiccator it is weighed in a covered capsule. It contains, according to Finkener, 3·794 per cent P_2O_5—

$$\left(=\frac{1}{26{\cdot}352}\right).$$

The formula requires 3·78 per cent—

$$\left(=\frac{1}{26{\cdot}46}\right).$$

The percentage of P_2O_5 in the residue is regularly rather less. The proportion of P_2O_5=3·72 per cent—

$$\left(\frac{1}{26{\cdot}90}\right)$$

can, indeed, not be regarded as quite decisive, on account of the very small quantities employed; but from a number of weighings there appears a rather lower value, a mean of 3·753 per cent—

$$\left(=\frac{1}{26{\cdot}65}\right),$$

which borders very closely on the demands of theory.

2. *Methods for the Indirect Measurement of the Ammonium Phosphomolybdate.*

The following indirect methods result from the experiments above given:—

Saturation with Alkali.—a. The precipitate, after being washed with a cold, neutral 5 per cent solution of ammonium nitrate, is placed in a beaker along with the filter, and diffused as uniformly as possible by stirring with a glass rod. In order that there may be no subsequent loss of ammonia, the volume of the water must not be less than 30 c.c. to 0·010 grm. P_2O_5. A few particles of phenolphthalein are added, and standard soda-lye is run in, constantly stirring till the liquid takes a decidedly red colour. When all the precipitate is dissolved we titrate rapidly back with nitric acid until all colour has disappeared. If in consequence of a slight reduction there remains a bluish colouration, a transition from reddish to greenish blue marks the limit of neutrality.

For neutralising the mol. of ammonium phosphomolybdate there are required 23 mols. NaOH.

1 c.c. of a decinormal soda-lye (=0·008 grm. NaOH) represents 0·016322 grm. ammonium phosphomolybdate, 0·00061739 grm. phosphoric acid, and 0·015026 grm. molybdic acid.

b. The precipitate, freed from acid by washing, is, as above, distributed in water and dissolved in a measured volume of dilute soda or sodium carbonate. The liquid is tinged with a trace of phenolphthalein, and titrated with decinormal acid until the colour disappears. Another equal volume of the alkaline liquid is measured and titrated with the same acid. Of the excess of acid consumed in the second experiment, 23 mols. represent 1 mol. ammonium phosphomolybdate.

The author has not tried this latter method.

Precipitation from a Neutral Solution by Nitric Acid.—The washed precipitate is dissolved in ammonia, the liquid mixed with ammonium nitrate (about 10 per cent), accurately neutralised, and titrated with nitric acid until complete precipitation is effected, using the precautions laid down above; or the neutral solution is thrown down with

* The use of the air-bath for drying the total solids is essential if results are needed in reasonable time, taking care, however, that the temperature never exceeds 100° C.

an excess of standard nitric acid, filtered, washed with solution of ammonium nitrate, and the excess of nitric acid is determined in the filtrate. The difference represents the acid consumed in precipitation. About 26 mols. precipitate 1 mol. ammonium phosphomolybdate (see section 4).

One c.c. $\frac{n}{10}$ nitric acid = 0·0126 grm. NO_3H, represents 0·01444 grm. ammonium phosphomolybdate, 0·00054616 grm. phosphoric acid, and 0·0132923 grm. molybdic acid. —*Zeitschrift fur Analytische Chemie*, vol. xxviii., p. 141.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending September 30th, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To General A. De Courcy Scott, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, October 9th, 1889.

Sir,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 175 samples examined were found to be clear, bright, and well filtered.

It will be seen that during the month of September the supply of water to the Metropolis has fully maintained the satisfactory character taken note of in our two previous monthly reports.

The supply for the past three months has been characterised by presenting a notable uniformity of composition throughout; as is especially shown by a comparison of the results furnished by the water distributed by the Companies taking their supply from the Thames.

Thus the several mean amounts of oxygen required to oxidise the organic matter present in a gallon of the Thames-derived water, were found to be 0·040, 0·037, and 0·34 of a grain, in the months of July, August, and September respectively.

Similarly the mean amounts of organic carbon present in the successive months' supplies were found to be 0·137, 0·138, and 0·138 part respectively in 100,000 parts of the Thames-derived water; while the maximum amount of organic carbon met with in any single sample examined in July was 0·153 part, in August 0·151 part, and in September 0·148 part in 100,000 parts of the water, these maximum proportions of organic carbon corresponding as nearly as may be to but just over a quarter of a grain of organic matter per gallon.

Having regard, however, to the seasonal fluctuations in composition, for the most part indeed within a very narrow range, to which river-water is liable, a continuance of such low and uniform results as those above recorded is hardly much longer to be expected.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 207).

Appendix.

I. *Chemistry in the London Board Schools.*†

The teaching of chemistry in the London Board schools calls for special remark, in view of the comprehensive scheme of "systematised object lessons, embracing in the six school years a course of elementary instruction in physical science, and serving as an introduction to the science examinations which are conducted by the Science and Art Department." This system has been in vogue for some years and constitutes the optional subject—"elementary science"—of the Code. It is continuous with the object lessons of the infant schools, and bridges over the usual gulf between these and the "specific" science subjects. The following is a model scheme suggested by the School Management Committee of the London School Board:—

Standard I.

Extension of the object lessons in the infant school, with simple illustrative experiments.

Standard II.

Comparison of different plants or animals.
Ordinary phenomena of the earth and atmosphere.
Substances of domestic use.

Standard III.

Simple principles of classification of plants and animals.
Further phenomena of the earths and atmosphere.
Substances used in the arts and manufactures.

Standard IV.

More complete classification of plants and animals, with typical examples.
The three forms of matter familiarly illustrated.

Standard V.

(*a*). Animal and plant life, with the most useful products;

or,

(*b*). More definite notions of matter and force illustrated by simple machinery or apparatus.

Standard VI.

(*a*). Animal and plant life, with special reference to the laws of health;

or,

(*b*). The commonest elements and their compounds.
The mechanical powers.

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

† For this information I am much indebted to Dr. J. H. Gladstone, F.R.S.

Standard VII.

(*a*). Distribution of plants animals, and the races of mankind;

or,

(*b*). Light, heat, and electricity, and their applications.

The scheme is adopted wholly or partially in a considerable number of London Board schools. It is encouraged by the Board providing the rarer objects and offering a museum cabinet to any school in which a good commencement of a collection has been made. It will be seen that the course of instruction embodies a considerable amount of elementary chemistry.

The teaching of chemistry as a specific subject calls for no special remark. It is only adopted in ten schools, and no special teachers are provided.

The systematic teaching of mechanics ("in a large sense") by four peripatetic demonstrators is a very important feature in London Board schools. "The science demonstrator gives a lesson fortnightly to the boys in the fifth and higher standards, the lesson being illustrated experimentally by specimens and apparatus carried from school to school." This system is being widely adopted in the London School Board district, but it is scarcely yet beyond the experimental stage. Its prevalence accounts largely for the small amount of chemical teaching, but this is also attributed to the fact that chemistry is not of the same relative importance in London arts as in those of other large towns.

At the annual examination in 1888, 341 pupils passed in chemistry as a specific subject out of an average of 51,214 boys and girls in attendance on one or other of the fourteen "specific" subjects, or a total of about 420,000 children on the school registers.

In the evening schools chemistry is taught on the lines of the South Kensington syllabus, but only to a very slight extent, the number in attendance not exceeding 100 in 1887—1888.

In the pupil-teachers' schools chemistry is also taught according to the syllabus of the elementary or alternative elementary stage of South Kensington.

II. *Chemistry in Birmingham Board Schools.*

In the thirty-four Birmingham Board schools, with average attendance of 38,000, all boys receive instruction in "Elementary Science" in Standards V. and VI. Thus 2700 boys learn mechanics, 550 magnesium and electricity. 2200 girls learn portions of chemistry and physiology under the name of Domestic Economy. The instruction is given by a peripatetic demonstrator and four assistants, who give a lesson once a fortnight to each school. The lesson is recapitulated by the class-teacher, and the children reproduce it in a composition.

The teaching of chemistry as a distinct subject begins in a central Seventh Standard school, in which there are 200 scholars, with a head-master and five assistants.

In May, 1887, at the South Kensington examinations, 110 scholars were presented in theoretical inorganic chemistry, of whom only seven failed; in practical inorganic chemistry 112 were presented, 17 failed.

III. *Chemistry in Manchester Public Elementary Schools.*

(From a return issued by the Manchester Branch of the National Association for the Promotion of Technical Education).

Day Schools:—

Chemistry as a "specific" subject.—

Board schools	159 scholars.
Voluntary schools	5 "
Total	164

Chemistry as a science subject (under South Kensington).—

	Inorganic (theory).	Inorganic (practical).	Organic (theory).	Organic (practical)
Board schools ..	447	424	40	40
Voluntary schools	23	—	—	—
Total	470	424	40	40

Evening Schools:—

Chemistry as a science subject (under South Kensington).—

	Inorganic (theory).	Inorganic (practical).	Organic (theory).	Organic (practical).
Board schools ..	262	206	39	28
Voluntary schools	47	23	—	—
Total	309	229	39	28

Probably not less than 1000 pupils are receiving instruction in chemistry in these public elementary schools.

The teaching is in higher-grade schools, and also by means of peripatetic demonstrators.

There is laboratory accommodation provided by the Manchester School Board for 184 students; by the Salford Board for 70.

IV. *Chemistry in the Grant-earning Public Schools of Scotland.**

So far as science-teaching is concerned, the provisions of the Scottish Education Code are similar to those of the English Code.

Very little "elementary science" appears to be taught, and in chemistry, as a specific subject, only 350 scholars obtained grants in 1888—1889.

A considerable amount of teaching is done in connection with South Kensington, but I have been unable to obtain exact statistics.

There are no higher-grade Board schools in Scotland, as the Scotch School Boards have the control of many old-established secondary schools, such as the High Schools of Edinburgh and Glasgow. In some of these efficient instruction is given in special sciences.

The Technical Education (Scotland) Act of 1887 is so far a dead letter.

V. *Teachers of Chemistry in Public Elementary Schools and their Training.*

The following classes of teachers are recognised by the Education Department:—

Pupil teachers, assistant teachers, provisionally certificated teachers, certificated teachers, teachers of evening schools, and, by the Science and Art Department, science teachers.

It has already been stated that teachers of "elementary science" in the first four standards need not have passed any examination in science, nor are the inspectors enjoined to inquire particularly into the previous training of such teachers.

As to chemistry as a specific subject, the inspectors are instructed that it will be desirable for them to ascertain that the teacher has given proof of his fitness to teach by having acquitted himself creditably at a training college or at some other public examination.

The chemistry teaching in training colleges† is under the regulations of South Kensington. The students, unless possessing previous knowledge of the subject, are intended to have two years' training, of which instruction in practical chemistry and the performance of "the more important and characteristic of the experiments" are a necessary part. In December of each year an examination is held, on the results of which all payments on behalf of instruction in science in training colleges are made. This examination is based on the syllabus of the ordinary May examinations; but the standard is some-

* I am indebted to Professor Carnelley for information on this subject.

† *I.e.*, colleges for teachers in public elementary schools only.

what higher, and special questions are set on the method of teaching. Students who pass on the advanced paper or in honours are registered as qualified to earn payments on results.

At Christmas, 1887, 297 students in training colleges presented themselves for this examination in inorganic chemistry, of whom 76 passed in the first division, 172 in the second division, and 49 failed. In practical chemistry, of 190 candicates, 47 obtained a first class, 96 a second class, and 47 failed.

Any person over eighteen years of age approved by the inspector may become a teacher in evening schools.

The simplest qualification for a teacher of chemistry as a science subject under South Kensington was, until recently, the obtaining of a second class in the advanced stage at the May examinations in that subject. This is now raised to a first class. The other qualifications considered equivalent by the Department need not be enumerated, except the most important one, viz., that the teacher has been trained at the Normal School of Science and Royal School of Mines. For details of the curriculum reference must be made to the Science Directory.

Certain grants and privileges are allowed to science teachers who have proved themselves specially meritorious. These are briefly—

(*a*). Payment of railway fare and £3 to attend a free summer course of lectures at South Kensington; or,

(*b*). Free admission to the classes of the Normal School of Science, railway fare, and 21s. or 30s. per week whilst in attendance; or,

(*c*). Part payment (½ for day classes, ⅓ for evening classes) of fees for classes taken at university colleges by selected teachers; or,

(*d*). Payment of expenses of a teacher taking a group of towns or villages; or,

(*e*). Admission of qualified teachers to classes at South Kensington at a fee of £1 for each subject.

In the session 1886-7 there were at the Normal School of Science twenty-four teachers in training taking chemistry, in addition to a larger number of regular students, who will become eventually science teachers. Forty-seven science teachers attended the summer course in chemistry.

Forty-two teachers were selected to attend classes at university colleges, of whom only a part took chemistry.

In addition to the above methods of training teachers, school boards may themselves institute special classes. Thus in Leeds there has been during the past year a class for the instruction of elementary teachers and one for pupil teachers in theoretical and practical chemistry. Instruction was given by the science demonstrator to the School Board, and the attendance was 30 in the first class and 12 in the second. It would be very difficult to obtain complete statistics of the amount of this kind of teaching that is in operation throughout the country, but it does not appear to be very general.

VI. *The Teaching of Chemistry in Evening Schools under the Education Department.*

The chief points in which the administration of evening schools differ from that of day schools are as follows:—

1. No pupils may be presented for examination below the third standard.
2. In the third or fourth standard the first subject additional to the three R's must be English, and, if a second be taken, it must be geography or elementary science.
3. Above Standard IV. scholars are unrestricted in their choice of additional subjects.
4. A fixed grant of 4s. is made on the average attendance if the class has met not less than forty-five times and of 6s. if not less than sixty times.

A grant of 2s. is made for every pass in an elementary or additional (*i.e.*, class or specific) subject.

The total number of scholars on the register of evening school in 1887-8 was about 50,000, of whom about two-fifths were in Board schools and three-fifths in Voluntary schools. One-seventh of the scholars were under fourteen years of age, and one-twentieth twenty-one and over. Nearly four-fifths were qualified for examination. About 1200 passed in two additional subjects (*i.e.*, they may have taken a science subject).

More detailed returns are not published, but probably it is safe to say that less than 500 evening scholars took chemistry as a specific subject. This shows that the teaching of chemistry to evening scholars is almost entirely under the Science and Art Department.

VII. *Recommendations of the Royal Commission on Technical Instruction (Report 1884) affecting Chemical Teaching in Public Elementary Schools.*

The Commissioners recommend—

(*a*). That science be given a more favourable position under the code by a reduction of the number of "class" subjects to two in the lower divisions of schools, one of which shall be elementary science, including geography.

(*b*). That school boards have power to establish, conduct, and contribute to science classes for young persons and artizans under the Science and Art Department.

(*c*). That the teaching under South Kensington be made more practical in the higher stages and be subject to more thorough inspection; that payment of fees be not necessarily demanded from artizans, and that the building grants be not limited to £500.

(*d*). That the teaching of science in training colleges be made more efficient and subject to better inspection, and that greater facilities be given for the students to pass on to the Normal School of Science, or other place for higher scientific instruction.

(*e*). That secondary, "modernised," and technical schools should be established out of ancient endowments and by contributions from "local authorities."

VIII. *The Technical Education Bill* (1889) *and the Teaching of Chemistry in Public Elementary Schools.*

This Bill, introduced by Sir Henry Roscoe on behalf of the National Association for the Promotion of Technical Education, would, if passed in its present form, make the following changes:—

(*a*). School boards or *local authorities*, or *both*, would be enabled to establish day or evening classes and provide laboratories, apparatus, and collections, &c., for the teaching of chemistry in public elementary schools *and to maintain them from the "local rates,"* with aid from the Education or Science and Art Department, or both, under conditions to be defined by special minutes of the departments. Admission to such classes *would not necessarily be restricted to children above the fourth standard*, although power is given to impose an entrance examination in reading, writing, and arithmetic.

(*b*). School boards or local authorities might also contribute directly or by payment of the fees of deserving students, or by means of scholarships to the aid of the teaching of chemistry *in any elementary, secondary, or technical school or in a college*, and grants in aid would be obtainable by schools from the Science and Art Department.

(*c*). Chemical instruction provided under this Act in public elementary schools would be under the inspection both of the Whitehall and South Kensington inspectors.*

* The important innovations are italicised.

The Technical Education Bill would thus affect the teaching of chemistry favourably as regards secondary and higher instruction, enabling the school boards and local authorities to make direct contributions to mechanics' institutes, technical schools, grammar schools, and colleges, as well as to their own technical classes in elementary schools. It is difficult to say how far it would affect the teaching of chemistry in *bonâ fide* elementary schools; but it seems to aim either at encouraging the optional subject, elementary science, and the specific subject, chemistry, and increasing the grants on them indirectly, or at enabling children to receive chemical instruction of the South Kensington type in the early standards irrespective of the three R's. If the Bill passes in its present form, there will apparently be three ways of taking chemistry in an elementary school, viz., (1) as a specific subject under the Whitehall Department; (2) as a science subject under South Kensington; (3) as a technical subject under both. The educational aim is the same in all three cases, and it seems a great pity that the small amount of simple science teaching that is required for children in legitimate elementary schools should be so complicated in administration. It would seem that a simple alteration of the code is required to give a proper basis for technical instruction, and that a technical or secondary instruction Bill would be more fittingly limited to technical and secondary schools.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology; or, Chemistry in its Applications to Arts and Manufactures. Edited by C. E. Groves, F.R.S., and W. Thorp, B.Sc., with which is incorporated "Richardson and Watts' Chemical Technology." Vol. I. "Fuel and its Applications." By E. J. Mills, D.Sc., F.R.S., and F. J. Rowan, C.E. London: J. and A. Churchill.

We have here a book not merely valuable, but admirable, from the patience and erudition shown by the authors in collecting the materials, as well as from their judgment in elaborating the vast mass of matter which has been in their hands. Nor must we overlook the number, the appropriateness, and good execution of the illustrations.

As regards the history of the work, its basis is a German treatise well known as "Knapp's Technology." An extended, and English, edition was brought out by Richardson and Ronalds, and was again much enlarged and in great part re-written by Richardson and Watts.

The present work is, however, necessarily to a great extent a new departure, and is divided into a number of sections, of which the present volume, on "Fuel and its Applications," forms the first. The authors here discuss the subject generally, the special employment of fuel in the various chemical arts being reserved for subsequent volumes. The justice of opening a work on chemical technology with a study of the means of producing or applying heat will be apparent if we remember that of old the chemist was termed the "philosopher *per ignem*."

The authors, after introductory generalities on fuel, consider in succession wood, peat, coal, the effect of heat on fuels, wood, charcoal, coke, peat-distillation, artificial fuel, gaseous combustibles, liquid fuel, minor fuels, theory of heat, flame, the application of fuel, domestic heating, heating by hot air, hot-blast stoves, heating by water and steam, the application of fuel to vaporisation, evaporation, distillation, drying, bakers' ovens, brick and porcelain kilns, furnaces, gas furnaces, the practical effect of fuel, concluding with analytical tables of various kinds of coal and other fuel, and with an appendix on coal-washing.

In the account of areas of coal in different countries, and in the remarks on its quality, we find certain omissions which are to be regretted. There is no mention whatever of the coal-fields of Natal, and of other parts of South Africa, although these are understood to be considerably more extensive than those of Britain. There are analyses of the coal of Tasmania, New South Wales, and Borneo, the Labuan kind (here by a typographical error given as Lahman), but there is no mention of the extent of the fields. There are likewise a number of analyses of New Zealand coal but with a similar omission. The same applies to the coal of India. This is unfortunate, since the coal-producing capabilities of the British empire naturally concern the reader more than those of the European Continent, or of the United States, concerning which there is a plethora of information. On the coal-fields of China we can find no data. Now, as the deposits in that empire are reported to exceed in extent even those of America, we hoped to find here trustworthy data. The coal of Saghalien, which has been seized by Russia on this very account, as well as that on the Amur and in Corea, have been found unfit for steam purposes. Hence it is possible that the Chinese coal may prove to be of similar quality.

On the luminosity of flame we find an interesting account of the most recent results. It is well known that Dr. Frankland called in question the old theory of the luminosity of flame, and ascribed it as, in many cases at least, due to the existence of a high temperature, and to the presence of gases and vapours of great density. This, however, according to the more recent investigations of Soret and Burch, is not invariably the case. The luminosity of a candle flame is, at all events, due to intensely ignited solid matter. It has been found that when the image of the sun was projected, by means of a lens, on the flame of a candle a spot of light appeared, and this light, when examined with the spectroscope, showed distinctly all the Frauenhofer lines. When examined by means of a Nicol's prism the light was found to be completely polarised at right angles to the line of incidence, proving that it was reflected from solid particles.

As regards liquid fuel we find no expression of opinion as to its origin. It is said that the Kimmeridge shales, of Dorsetshire, of which there is practically an unlimited supply, yield 40 gallons of crude oil per ton. So far, however, as we have come in contact with this product, we have found it of a most evil odour, whence we fear that its satisfactory purification would prove expensive.

The subject of natural gas receives full attention. At Pittsburg it has been found that 1000 cubic feet of gas was equivalent to 81⅛ lbs. of coal. But the coal in question is worth only 5s. per ton, so that the fuel value of the natural gas, if it is to compete with coal, must not be above twopence per 1000 cubic feet. Hence, the expense of winning, piping, and managing, and gas-supply must be very low if it is to yield a profit upon this valuation. For metallurgical purposes it has the advantage of being free from sulphur.

The advantages, or disadvantages, for domestic lighting purposes of the so-called "water-gas" are not here discussed. But the analyses quoted show a very considerable variety in its composition, according to the process used. The dangerous ingredient, carbon monoxide, may reach 28, 31, or even 35 per cent.

Among other important questions here dealt with, but which space does not permit us to notice, are the more complete recovery of the nitrogen present in coal, the elimination of sulphur from coke, the recovery of the oily and tarry matters given off from coke-ovens, the remunerative treatment of peat, &c.

To competent men this book will carry with it its own urgent recommendation.

Watts' Manual of Chemistry, Theoretical and Practical (Based on Fownes' Manual). Vol I. Physical and Inorganic Chemistry. Second Edition (Fourteenth Edition of Fownes'). By W. A. Tilden, D.Sc., F.R.S., Professor of Chemistry in the Mason College, Birmingham. London: J. and A. Churchill.

"Fownes' Manual" has long, and with full reason, been a general favourite among teachers and students, as will be at once seen from the fact that the present is the fourteenth edition. In the successive hands of Watts and of Dr. Tilden it has undergone such additions, emendations, and general modifications as the rapid growth of chemical science demand, and we have full reason for asserting that in its present form it will be even more highly valued than its predecessors have been.

Among the principal alterations in this edition we note the suppression of the section on Physics. Much of the matter which it contained is incorporated with the text in appropriate parts of the work, and for fuller instruction the student is referred to special physical text-books, of which there is now no lack.

There has also been introduced, apparently in accordance with the original intention of Fownes, a series of systematic directions for an elementary course of experiments.

The recent results of research, wherever they can be regarded as definitely established, have been fairly brought forward. As instances of this the reader is referred to the sections on the Periodic Law, the Spectroscope as an Instrument of Chemical Investigation, and on the Rare Metals. Generally speaking, we are surprised at the quantity of information which has been condensed into this volume, and that without any sacrifice of clearness.

We are much pleased at the total absence of all reference to examinations. The editor's great object has been not that the student should "pass," but that he should know. We can only express our confidence that the work will be appreciated as it unquestionably deserves.

Outlines of the Clinical Chemistry of Urine. By C. A. MacMunn, M.A., M.D. (Dublin). London: J. and A. Churchill.

The object of this work is to present the chemistry of urine in health and in disease in a form calculated to suit the requirements of the medical practitioner.

The author sets out with an account of the function of the kidney and the mechanism of its secretion. In the second chapter we have an account of the general characters of normal human urine, followed in the next chapter by a description of the constituents of normal urine, and instructions for the estimation of urea by Liebig's process and by the hypobromite method. For the determination of total nitrogen Pflüger and Bohland's modification of the Kjeldahl process is recommended. The methods of J. A. Wanklyn for determining urea and nitrogen are not mentioned.

In the succeeding chapters we find descriptions of uric acid and allied bodies, such as allantoin, creatinin, xanthin, &c., the non-nitrogenous organic acids, the aromatic bodies, and colouring matters of urine. Here the author describes a pigment giving a very characteristic absorption-spectrum, and which he has named "urohæmatoporphyrine."

Among the inorganic constituents of urine hydrogen peroxide is mentioned, on the authority of Schœnbein. There is also a notice of a condition known as phosphaturia, on the recognition of which Dr. MacMunn lays more weight, as it is misinterpreted by quacks to the great alarm of their unhappy patients.

The second part of the work treats of the abnormal constituents of urine, serum, albumen, and other proteids, blood and bile, sugars, acetone, and diacetic acid, fatty bodies, crystine, tyrosine, leuceine, and oxymandel acid.

The concluding part of the work is devoted to urinary deposits and calculi and the detection of various drugs or poisons in urine.

The instructions for the determination and estimation of the constituents of urine, normal or abnormal, are fully on a level with the science of the day, and will render this work a valuable book of reference for the faculty. We are pleased to find here a chart of the absorption-spectra with the necessary explanations.

Service Chemistry; Being a short Manual of Chemistry and its Applications in the Naval and Military Services. By Vivian B. Lewes, F.I.C., F.C.S., Professor of Chemistry, Royal Naval College, Greenwich. London: Whittingham and Co.

This work is a new departure. Chemistry has, of course, weighty words to say in military and naval affairs, as, indeed, in almost every department of human activity. But, in the English language at least, no systematic attempt has been made to call attention to such lessons.

The author, rightly enough, says that there is but one chemistry, and that its technical adaptation to any special subject is merely an amplification of the science in one particular direction. Still, it strikes us that the officers and others, for whose use this work has been specially arranged, might have been more advantageously referred for general principles to some one of the many chemical manuals now in existence.

The subjects principally noticed are fuel, explosives, drinking-water, boiler incrustations, corrosion and fouling of iron ships, paints, ventilation, &c. The instructions given concerning drinking-water seem to us scarcely sufficient; nothing is said concerning the analysis of waters with a view to the detection of doubtful or injurious ingredients, organic or inorganic. Now, such information must be very necessary for troops on the march, or during a campaign. For want of better knowledge, too, the captain of a ship may fill his tanks with bad water.

Directions for Clarkising and filtering impure water are given very carefully and at some length. The comparative effects of animal charcoal and of "carbalite" upon Thames water have been tested in a series of special experiments. It appears that the charcoal was rather the more effective in removing "total solids" and chlorine, but that carbalite had the advantage as far as "free" and "albumenoid ammonia" are concerned. These experiments might have been usefully extended so as to include Anderson's scrap-iron filter, Bischof's spongy iron, and Doulton's manganous carbon. The author makes an indirect mention of the value of alum in precipitating organic matter held in solution in impure waters; saying that it is one of the ingredients of Maignen's "anti-calcaire," but the Chinese have used alum for this purpose for thousands of years. This process is much to be recommended under circumstances where filters of any size cannot be conveyed. It is merely necessary to put the water in a tub, add a few grains of alum, stir up, and let settle. The clear liquid above may then be drawn off and used with safety, whilst the water without such treatment would prove highly dangerous. It must not be supposed that the absence of animal pollution proves that a water is safe. In some very scantily peopled districts the water of the springs may be very seriously polluted, as some savage tribes, both in Africa and America, have the abominable custom of burying their dead beneath springs and shallow streams.

The behaviour of different kinds of water when used for raising steam receives due notice. In this connection the author points out that if animal or vegetable oils—any other than mineral—are used for lubrication they are split up by the superheated steam, and the fatty acids being set free, corrode the boiler plates.

As regards the prevention of incrustation the author

thinks that in the case of marine engines no agent added in the boilers gives satisfactory results. The water should undergo a suitable treatment before being pumped into the boilers. For land engines, where only hard water is to be procured, he prefers sodium carbonate or paraffin oil. Animal and vegetable oils and fats he very justly condemns altogether.

In connection with the production of saltpetre we find mention of a curious fact observed by the late Professor Bloxam, viz., that "the urine of a man would furnish 2 ozs. of saltpetre daily, an amount sufficient to make nine rounds of small-arm ammunition."

Mr. Lewes is to be congratulated on the general idea of this book, as he will easily be able to eliminate its defects in future editions.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lx., p. 208) "The Writer of the Report" (which appeared in vol. lx., p. 157) asks me, in the interests of science, to give the composition and properties of my reagent, and to explain the *rationale* of its formation. To this invitation I shall gladly respond as soon as certain investigations now in progress are completed.

What the writer of the report calls a very serious mistake in my "Notes Relating to the Demonstration at Wimbledon," only appears so to him in consequence of misapprehension. I do not for one moment dispute that other sludges may be inoffensive, even when first drawn from the tank; but does the writer of the report know of any which would, like that from the "Amines" process, keep inoffensive if tipped on to land without further treatment, and exposed during the summer months to alternating sunshine and showers? Since this involves my chief claim, namely, sterilisation, in other words, complete and permanent disinfection, would it be too much to ask the writer to name the process, or processes, to which he alluded?—I am, &c.,

HUGO WOLLHEIM, Managing Director.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
October 29, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 15, October 7, 1889.

New Observations on the Reciprocal Displacements between Oxygen and the Halogens.—M. Berthelot.—This paper will be inserted in full.

Facts towards the History of Raffinose.—M. Berthelot.—Raffinose presents itself in two different forms according to the conditions of its crystallisation. When it is caused to crystallise from alcohol it is generally obtained in small hard granulated crystals containing 15·1 per cent water of crystallisation. This is the ordinary form described by Loiseau, Scheibler, Ritthausen, and Tollens. It answers to the formula $C_{36}H_{32}O_{32} + 5H_2O_2$. The author has also obtained it in another form from aqueous alcohol containing from 17 to 18 per cent of water, and agreeing with the formula $C_{36}H_{32}O_{32} + 6H_2O_2$. Possibly there exists also a third hydrate containing $4H_2O_2$.

Synthesis of Certain Oxygenated Selenium Compounds belonging to the Aromatic Series.—C. Chabrié.—The author first tried to oxidise phenyl selenide directly by nitric acid, potassium permanganate, and chromic acid. With nitric acid he obtained nitro-products; with the two others no definite compounds were produced. On treatment with oxygenated water mixed with hydrochloric acid he obtained a body containing oxygen, but this element was fixed upon the phenylic nucleus and not combined with the selenium. Lastly, he caused the dichlorhydrine of selenious acid to react upon benzene in presence of aluminium chloride. According to the proportions he obtained diphenyl-selenine or its chlorine derivative.

Researches on Fucusol.—M. Maquenne.—The author shows that the fucusol of Stenhouse is a mixture of furfurol and methyl-furfurol in the proportion of ten parts of the first to one part of the second. The name of *fucusol* not applying to any definite proximate principle should therefore be abandoned. The molecular structure of methyl-furfurol has still to be determined.

On the Presence of Pectic Compounds in Plants.—Louis Mangin.—The author shows the presence of pectic compounds in vegetable membranes, where they are constantiy present, and more rarely in the cellular cavity, as in the leaves of yew, of *Calla æthiopica*, and in the flowers of the hyacinth.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., July, 1889.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—This paper is not adapted for useful abstraction.

The Methods and Procedures for producing Chlorine and Hydrochloric Acid by Means of Magnesium Chloride.—Dr. G. Eschelmann.—The author describes and criticises the processes of Schlœsing and of Weldon-Pechiney. He considers that the latter merits most attention, and expects that it will confer upon Stassfurt a monopoly of the manufacture of chlorine-products for the entire world.

The True Formula of the Permanganates.—Ch. Bradbury.—From the CHEMICAL NEWS.

Recent Synthetic Experiments in the Series of the Saccharine Matters.—E. H. Keiser.—From the *American Chemical Journal.*

Scientific and Industrial History of Aniline Black.—Prof. E. Noelting.—Already noticed.

Lecture Experiments on Nitric Acid.—P. Austen.—From the CHEMICAL NEWS.

The Use of Hydrogen Peroxide in Analysis.—Mr. Dunnington.—From the CHEMICAL NEWS.

The Great Chemical Industries at the Paris Exhibition.—P. Kienlen.—A list of exhibitors with brief notices of the articles displayed.

Green Ultramarine.—Dr. Szilazi.—From *Liebig's Annalen.*

On the New Metal, X, Extracted from Cobalt and Nickel.—Prof. G. Krüss and F. W. Schmidt.—Already noticed.

Industrial Society of Mulhouse.—Session of May 8, 1889.—M. Albert Scheurer sent in a paper on thioflavine, a new yellow basic colouring-matter manufactured by Casella and Co., of Frankfurt. It is soluble in water and in alcohol, very soluble in acetone, acetine, and acetic acid. It is readily fixed by means of tannin. The following colour gives good results on cottons:—40 parts thioflavine, 50 tannin, 50 water, 100 acetic acid, 60 acetine, and 700 gum water. Steam and pass through tartar.

ometic. It is nearly as bright as chrome yellow, resists light, and does not soil the whites.

Extraordinary Session, May 22, 1889.

The session was devoted to a revision of the list of prizes. H. Kœchin sent in a sample of an artificial textile fibre, dyed in rhodomie, more brilliant and beautiful than silk. The fibre is prepared at Lyon by a patented process from a solution of gun-cotton. It is much weaker than silk.

A New Series of Aluminium Compounds.—Already noticed.

Ferro-Manganese with a Low Percentage of Carbon.—Sergius Kern.—From the CHEMICAL NEWS.

MISCELLANEOUS.

University College Chemical and Physical Society.—On Wednesday, November 6, at 4.30 p.m., a paper will be read on "The Nature of Electricity," by A. H. Fison. D.Sc.

Appointment.—Mr. D.S. Macnair, Ph.D., F.C.S., &c., has been appointed by the Trustees Instructor of Chemistry in the People's Palace Technical Schools, London. Dr. Macnair, who has proved himself to be an excellent teacher, and also capable of carrying on original research, was very highly recommended by Sir Henry Roscoe, and by Professor Emil Fischer, of Würzburg.

Physical Society of Liverpool.—It is proposed to form a Physical Society in Liverpool, which will hold its Meetings at University College, and Professor Oliver Lodge has consented to be nominated as first President. The Preliminary Meeting will be held in the Physics Theatre of the University College, at eight o'clock, on Wednesday evening, November 6th, Professor Oliver Lodge in the chair. Local students and all others interested in the subject are invited to be present. The Secretary (pro tem.) is Mr. Thomas Tarleton, 1, Hyde Road, Waterloo, Liverpool.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 4th.—Society of Chemical Industry. "An Account of a Borax Lake in California," by C. Napier Hake.

—— Royal Institution, 5. General Monthly Meeting.

THURSDAY, 7th.—Chemical 8. "The Isolation of a New Hydrate of Sulphuric Acid existing in Solution," by S. U. Pickering. "Further Observations on the Magnetic Rotation of Nitric Acid of Hydrogen Chloride, Bromide, and Iodide in Solution," by Dr. W. H. Perkin, F.R.S. "On Phosphoryl Trifluoride," by T. E. Thorpe, F.R.S., and F. T. Hambly. "On the Acetylation of Cellulose," by C. F. Cross and E. Bevan. "On the Action of Light on Moist Oxygen," by A. Richardson. Anhydracetophenonebenzil and the Constitution of Linius Lepidens," by Drs. Japp, F.R.S., and Klingeman.

TO CORRESPONDENTS.

M. T. S.—The question is on "Avogadro's Law." See Kolbe's "Inorganic Chemistry," by Humpidge (Longman's), pp. 50, 575.

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

VOL. LX. No. 1563.

RE-EXAMINATION OF THE SPECTRA OF TWENTY-THREE GAS-VACUUM END-ON TUBES, AFTER SIX TO TEN YEARS OF EXISTENCE AND USE.*

By C. PIAZZI SMYTH, late Astronomer Royal for Scotland.

WHEN looking over lately, in the spectroscope, a number of end-on gas-vacuum tubes, of ages between six and eleven years, and by diverse makers in Paris, London, and Edinburgh, the too usual impurity of hydrogen lines was found abundantly in almost all of them; while even still more noticeably there were seldom any two where the relative intensities of the principal lines of both high and low temperature hydrogen ranged exactly together through a large part of the spectrum.

But intensity of light, whether relative or absolute, so long as it keeps within moderate limits, is of very small importance in spectroscopic research; while, on the other hand, the question of the absolute spectral place of a line, or the spectral distance of one line from another, is a fact of most crucial value, no matter to what excessively small extent any change therein may be established under particular circumstances. In cases, then, where the intensity of the lines has changed *much*, may their spectral places have changed a *little*; and if the general belief is to the contrary, has that impression been arrived at by theory, or from the result of careful micrometrical measures? And, either in one way or the other, has it been positively proved that hydrogen gas may not sometimes be modified in its spectral action, when shut up in an attenuated state, in a glass tube with a larger amount of some other gas for several years, and provoked through the greater part of that time by electric sparking to form some possible combination with its neighbour?

Enquiry by practical experiment seemed to me, with measuring apparatus in hand, the best answer to attempt, though it was not very hopeful, as my dispersion power available at the time was not great. But the case seemed at least worth trying, if only to be thereby authoritatively laid on the shelf again, and the spectroscope set free for other work.

Starting then with four tubes prepared in three countries positively for pure hydrogen and nothing else, three of their high and one of their low temperature lines, forming together a well-stepped and fiducial series between red at one end and violet at the other, were chosen and micrometrically measured again and again in spectrum place, both direct and reversed, as well in the tube's position before the slit as in direction of current, but without alighting on any anomaly. In fact every one of these tubes of intended hydrogen gave exactly the same spectrum of place for its lines as every other; so that each formed an invaluable scale of place-reference for the lines of any unknown or suspected incandescent gas.

Next were examined in the same apparatus—

Two	tubes	of carbonic oxide	with	hydrogen	therein.
One	,,	chlorine	,,	,,	,,
One	,,	cyanogen	,,	,,	,,
One	,,	hydrochoric acid	,,	,,	,,
One	,,	iodine	,,	,,	,,
One	,,	nitrogen	,,	,,	,,
One	,,	nitrous oxide	,,	,,	,,
Two	,,	olefiant gas	,,	,,	,,
Three	,,	oxygen	,,	,,	,,
Two	,,	mercury	,,	,,	,,

* Read before the British Association, Section A, Newcastle Meeting.

Although in all these tubes hydrogen lines were found in various intensities, yet all the closest measures, and in all the opposite positions possible for the tubes, failed to bring out any alteration of spectroscopic distance apart, as between any of the test lines shown by the smallest quantity of adventitious hydrogen in another gas's tube, and the same lines in any of the previous tubes of nothing but hydrogen. So that the electric spark would seem, where hydrogen is concerned, rather to preserve its purity than to promote its combination with something else present at the time; the sparks being confined to 1·5 inches in length, but the pressures at which the gases were included under hermetic seal varying from 0·05 to 0·50, 1·00, 2·50, and in one case even 4·00 inches of the barometer.

Other circumstances, however, that were not being looked for supervened, and fully repaid all the trouble spent as above in proving a negative, so far as such could be proved with a dispersion power of only 6·23°, and a magnifying power of no more than 15, but with exquisite definition.

These other circumstances were chiefly the progress of change in certain of the tubes subsequent to 1880, of one of which it was said and printed in 1880 that "it still shows its chlorine lines, but they are becoming fainter; while carbon bands and hydrogen lines have appeared, making its spectrum look very like what that of hydrochloric acid was at first." This chlorine-intended tube then, still testifying at that time for chlorine, has now, in 1889, nothing but hydrogen lines to show, and so brightly as to raise the question whether the chlorine can have changed into hydrogen within the walls of hermetically sealed glass.

Towards this end, however, we may derive some furthur and more unexpected information from a certain iodine tube of 1878: of which tube it was printed in the *Transactions of the Royal Society (Edinburgh)*, 1880, that, "it heats unduly beneath the spark, as if inclined for a change, and has much deposited haze in the interior. But no perceptible alteration of spectrum has yet been noted; and because, perhaps, the maker, M. Salleron, in Paris, put so large a quantity of solid iodine inside, that there is no chance of its all being dissociated, or converted into something else by weak sparks, only one inch long, within any moderate time—if iodine is really, as some persons are beginning to suspect, not the elementary body which chemists have long believed, but a compound."

Now at that date, 1880, that iodine tube was showing no less than 148 iodine lines by measure between red and violet. Of those lines, necessarily of low electric temperature, no less than 50 were identified with the high temperature spectra of the greater observers of iodine, and included all its strongest lines, twelve of them being exceedingly strong and brilliant. And it was further written at that time that this tube's spectrum is most peculiar for its freedom from nearly all known impurities of other gases—*save* three exceedingly faint reproductions of the three chief hydrogen lines. Yet in the present year, 1889, there is not one iodine line left in that tube, and its spectrum range is filled with nothing but both low and high temperature hydrogen lines of astonishing brilliancy. While of the large amount of iodine granules hermetically sealed into the tube in 1878—only a very small amount of apparently inert dust is now left.

Whether this change is an infinitesimally small part of the progress of everything to turn into hydrogen, and for assisting thereby the whole solar system to explode some day into a so-called and spectroscopically bright-lined hydrogen star—I will by no means weary the Section by enquiring now. But if three minutes more can be allowed, I would beg leave to mention shortly something else that has also turned up in course of this investigation, and is of quite a comfortable character; viz., that the best of all the gas-vacuum tubes that have passed through my hands were made for me in London, and can, I suppose, be re-

peated there for all who choose to order them in an intelligent manner.

How much this means may be judged of by the fact that I was actually written to in wrathful terms by a South-Australian, whom I did not know, several years ago, because, forsooth, he, having on his own choice written to *some one* in London for examples of my "end-on" gas-vacuum, tubes received in due course a set of which he could make no use, by reason of their containing a medley of all or any gases. Wherefore he denounced London tradesmen generally, and declared that South Australia would soon be obliged to get on without them.

Now, however, I can inform all and sundry that out of eight tubes made for me by Mr. Charles Casella, the skilful son of the well-known Mr. Louis P. Casella, of Holborn, no less than five of them (viz., one of CO, two of N, and two of O) have stood the difficult test of being found, after six years' existence, in perfect freedom from any of that most insinuating of all gaseous impurities, hydrogen, and capable, therefore, of being studied for the lines of their intended gases under unusually favourable circumstances.

Clova, Ripon, July 25, 1889.

REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its seventh annual report.

During the year just closed three bibliographies have been published by the Smithsonian Institution.

A Table of Specific Gravity for Solids and Liquids. The Constants of Nature, Part I. (new edition, revised and enlarged). By Frank Wigglesworth Clarke. Washington, D.C., 1888. Smithsonian Miscellaneous Collections, No. 659. 8vo., pp. xi., 409.

This volume contains the specific gravities of 5227 distinct substances and 14,465 separate determinations, being more than twice as many as in the first edition with supplement.

Index to the Literature of Columbium, 1801-1887. By Frank W. Traphagen. Smithsonian Miscellaneous Collections No. 663. Washington, 1888. 8vo., pp. [iv.], 27.

This Index contains the threefold arrangement chronological, alphabetical by authors, and subject-matter. The abbreviations of Journal-titles are those adopted by the Committee on Indexing Chemical Literature, upon whose recommendation this index was printed.

A Bibliography of Chemistry for the Year 1887, by H. Carrington Bolton. Washington, 1888. Smithsonian Miscellaneous Collections No. 665. 8vo., p. 13.

Prof. Wm. L. Dudley, Vice-President of the Chemical Section of the A. A. A. S., has appended to his address on the Nature of Amalgams an Index to the Literature of the subject, which will be printed in the forthcoming volume of the *Proceedings* of the Toronto meeting.

We record the publication of the following index. Lists of patents relating to Soap and Candles in "Manufacture of Soap and Candles," by Wm. Brannt, Philadelphia, 1889.

Also:—An Index of Researches upon the Production of Ammonia from Atmospheric Nitrogen. By Ezra J. Ware. Published in *Proceedings Michigan State Pharmaceutical Association*, 1888; H. J. Brown, Ann Arbor, Mich., Secretary.

Reports of progress from several volunteer indexers have been received. Dr. Alfred Tuckermann has completed his Index to the Literature of Thermo-dynamics, except a subject-index to which he is putting finishing touches. He has also begun an Index to the Literature of the Chemical Action of Light, a subject suggested by the Chairman of your Committee.

The publication of this annual report is always followed by numerous applications for information, especially with respect to the method of indexing adopted by the Committee. These inquiries we may in some degree anticipate by repeating the statement that this Committee does not prescribe any standard nor dictate any system for volunteers to follow. Those interested in the work of the Committee would do well to examine the six reports already published, in which will be found suggestions for systematic indexing (1885), a complete list of indexes already printed under the auspices of the Committee (1887), and a list of "Abbreviations of Titles of Chemical Journals," intended to secure uniformity in references (1887).

The choice of subjects for indexing has generally been made by the volunteers themselves; in a few instances only the topics have been suggested by the committee, at the request of co-workers. These subjects, as shown in our reports, cover a wide range in physical, inorganic, and organic chemistry; the desirability of procuring indexes to individual elementary substances should not be overlooked by those who contemplate offering aid. A few copies of the Report of 1887 (which includes lists as above) remain, and can be had on application to the chairman, to whom, also, letters of inquiry may be addressed, care of Smithsonian Institution, Washington.

H. Carrington Bolton, *Chairman.*
F. W. Clarke.
A. R. Leeds (in Europe).
A. A. Julien,
John W. Langley.
Albert B. Prescott.
Chas. K. Wead.

* Advance proof from the *Proceedings of the American Association for the Advancement of Science*, vol. xxxviii.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Concluded from p. 219).

IX. *Recommendations of the Elementary Education Commission Report* (1888) *affecting Chemical Teaching.*

The recommendations in the recent report of the Elementary Education Commission are very favourable to science-teaching, as may be seen from the following extract:—

"If it be true, as we believe it is, that the object of elementary instruction is to give such instruction to the scholars in general as will best fit them to fulfil the ordinary duties of life to which they are most likely to be called, and to enable those who may be endowed with special gifts to rise to still higher callings, then elementary instruction in science—and we lay special stress upon the word "elementary"—is only second in importance to elementary instruction in reading, writing, and arithmetic. But the fact has impressed itself upon our minds that technical training does not exist for boys even to the extent that instruction in needlework and cookery supplies it for girls. We have had, however, a great deal of evidence showing the educative effect of science-teaching in elementary schools for both boys and girls; and we think that science, especially mathematical, mechanical, and physical science, is not only the foundation, but an essential part of thorough technical instruction.

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

"There are, however, certain broad principles to be laid down as necessary conditions of introducing science-teaching into elementary schools. In the first place care must be taken that it is not introduced too early in school life, lest it should interfere with the scholars' general instruction. In the second place we are of opinion that, as a rule, the ordinary elementary master cannot be expected to be a good science master. Even in the case of an elementary teacher who, while at the training college, has made good progress in science studies, we consider that he has so much also to do in the usual school routine, and that his attention is so much distracted from science, that he cannot be relied on either for clear, vivid, and simple lectures, or for neatness and certainty in the performance of experiments. But to possess the power successfully to achieve these results is an essential qualification in a science teacher, and especially so in one who has to expound experimental science to the class who attend our elementary schools."

In addition to general recommendations in the sense of the above quotation, the chief are—

(*a*). That object lessons should be continued in the lower standards in succession to similar teaching in the infant schools.

(*b*). That the system of peripatetic demonstrators should be encouraged.

(*c*). That more attention should be given to the possession of an adequate knowledge of natural science in the appointment of H.M. inspectors.

(*d*). That examinations in science should as far as possible be conducted orally, and not on paper, especially in the first five standards.

(*e*). That higher grades of elementary schools should be recognised as continuation schools.

(*f*). That technical instruction should be placed in the hands of, and mainly supported by, "local authorities," and be controlled by the Education Department.

(*g*). That the evening school system should be thoroughly revised so as to admit of (1) special curricula suitable to the locality; (2) attendance on "additional subjects" without at the same time taking the three R's; (3) attendance of scholars over twenty-one years of age. Also that a greater fixed grant should be awarded, and less be made to depend on individual examination.

X. *The New Proposal Code* (1889) *and Chemical Teaching.**

The chief changes contemplated in the new code are as follows:—

(*a*). The grant on results of examination in the three R's is cancelled, and the merit-grant disappears as a separate grant. The grants for elementary science and chemistry as a specific subject are, however, unaltered, *i.e.*, they are still based on results of individual examination.

(*b*). English is no longer compulsorily the first-class subject, and the position of elementary science is thus improved.

(*c*). Scholars of any public elementary school may attend science classes at any place approved by the inspector, and still earn Government-grants.

(*d*). Day-training colleges are recognised. Teachers of chemistry may thus be trained in the existing university colleges with a Government capitation grant of £35 per annum. The precise conditions are not yet defined. A third year of training is recognised for the first time.

(*e*). The conditions of age and grants are retained in evening schools, but a scholar who has passed Standard V. may be examined in "additional" subjects—*e.g.*, chemistry without the three R's.

These alterations, together with other minor ones, give greater freedom to the teaching in elementary schools, and especially influence the teaching of chemistry (1) by releasing the pressure due to the necessary individual "passing" in the three R's; (2) by making it possible for elementary science to be the first optional subject taken; (3) by allowing scholars to go outside for science instruction; (4) by making the chemistry-teaching in university colleges available for the training of teachers.

The code, however, as will be seen, falls short of the recommendations of the Elementary Education Commission so far as science teaching is concerned.

POSTSCRIPT TO APPENDIX.

The Technical Instruction Act (1889) *and Chemical Teaching.*

The Government Bill introduced and passed at the end of the recent session differs from Sir Henry Roscoe's Bill, referred to in the Appendix VIII., *ante*, in several respects. It provides mainly that the "local authority" (county or borough council, or urban sanitary authority) shall have power to contribute money to all schools and institutions not conducted for private profit in aid of all the sciences and arts relating to industries, and also in aid of manual instruction. The money is to be raised by a local rate not exceeding one penny in the pound in one year. The range of subjects of study and the relative aiding of different schools is to be regulated by the Science and Art Department. The effect of the Act will not be felt in the truly elementary schools, but it will greatly encourage the teaching of chemistry and other sciences to children who have passed the Standards.

From those who are engaged or interested in the teaching of physical science the Committee will be glad to receive any information which is likely to be of service in showing how their suggestions may best be carried into effect. It is requested that these communications be addressed to Professor Dunstan, 17, Bloomsbury Square, London.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

(Continued fom p. 213).

I HAVE now described the most important features of the electro-metallurgical industry as carried on at Milton, and will proceed to describe the chief properties of the alloys produced and some results obtained from them.

With copper, aluminium forms a series of interesting and beautiful alloys, varying in colour from bluish white to red gold and pale yellow, and also differing widely in physical and mechanical properties.

Alloys containing 60 to 70 per cent aluminium are very brittle, glass-hard, and beautifully crystalline; with 50 per cent the alloy is quite soft, but under 30 per cent the hardness returns. The 20 per cent bronze has a whitish yellow tint, and somewhat resembles bismuth; it is very brittle, and can be pulverised in a mortar.

The brittleness of alloys containing more than 11 per cent prevents their use, but from 11 per cent down to 1½ they are of very great value, possessing great tensile strength, high resistance to compression, low specific

* See article by Dr. Gladstone, "The New Code and Science-teaching," *Nature*, May 2, 1889; also statement issued by the National Association for the Promotion of Technical Education, "The New Education Code," 1889.

* Read before the British Association, Section B, Newcastle Meeting.

gravity, and greater resistance to corrosion than any alloy known.

The following gives the density of these alloys compared with other metals and alloys.

Metal.	Density.
Aluminium bronze 3 per cent	8·69
" " 4 "	8·62
" " 5 "	8·37
" " 7·5 "	8·00
" " 10 "	7·69
" " 11 "	7·23
Brass	8·38
Cannon bronze	8·23
Cast "	7·20
Cast steel	7·71
Iron	7·80
Nickel	8·57
Silicon	2·67
Platinum	21·50
Gold	19·30
Lead	11·40
Silver	10·50
Copper	8·90
Tin..	7·50
Zinc	7·10

The standard "A" grade, containing 10 per cent aluminium, behaves as a true alloy—that is, will not liquate out into different combinations. It resembles pale gold in colour; its tensile strength in castings runs from 75,000 lbs. to 90,000 lbs. to the square inch, with from 4 to 14 per cent elongation.

The following is the report of a test of 10 per cent bronze produced by the Cowles process, made by Prof. Unwin, and alluded to in his work on the "Testing of Materials of Construction," p. 348.

The bar was 0·499 in diameter, and was placed in shackles which have spherical bearing surfaces, so that the tension was extremely uniform on the section:—

Breaking weight 7·195 tons = 36·78 tons per sq. inch 86·743 lbs.

Elongation in 10 inches 3·326 inches = 33·26 per cent.

Contraction of area 0·078 inch = 39·87 per cent.

Elastic limit 3·47 tons = 17·74 tons per sq. inch.

The elongation in different parts of the bar was much more uniform than with iron or steel.

One-inch lengths measured after fracture:—

No. 1.	2.	3.	4.	5.	6.
1·27	1·27	1·26	1·28	1·27	1·26
7.		**9.**	**10.**	**11.**	**12.**
1·28	1·29	1·34	1·36	1·44	1·44

Test at Washington Navy Yard of Cowles Co. "Special Grade" Aluminium Bronze.

Specimens.	Dimension of specimen. Length in inches.	Diameter in inches.	Weight applied in lbs.	Elastic limit per sq. inch on original cross section.	Weight per sq. inch on original cross section.	Elongation per cent.	Reduction of area per cent.
No.				Lbs.	Lbs.		
1.*	2·00	0·500	22,485	—	114,514	0·45	0·00
3.	2·00	0·501	21,650	79,894	109,823	0·05	39

Ordnance Office, Navy Yard,
Washington, February 16th, 1886.

A. H. McCormick,
Commander, U.S.N., Inspector of Ordnance.

* Cu 89·0, Al 10·0, Si 1·0=100.

The high elastic limit in a material so plastic is noteworthy. In *resistance to compression* this metal equals the best cast steel; its *transverse strength*, or rigidity, is about forty times greater than ordinary brass; its limit of elasticity equals steel of the same tensile strength and elongation. Forged, tempered, and annealed, its elongation equals the best grades of steel of the same strength.

The "special" grade contains more aluminium than "A" grade; is higher in tensile, transverse, torsional strength, and elastic limit. Its elongation is less, ranging from nil to 8 per cent.

Accompanying was a test made at Washington Navy Yard, of metal of this grade, supplied by the Cowles Co.'s works (see preceding column).

Test Made in Leeds, England.

The Leeds Forge Co., Lim.,
Testing Department.

"Special Grade" Aluminium Bronze.

Nov. 10th, 1886.

Specimen.	Dimensions in inches. Diam.	Area.	Tensile strength in tons. Total per sq. inch.
1 round bar casting ..	0·285	0·0646	57·27 (128,400 lbs.)

For the Leeds Forge Co.,
(Signed) Sampson Fox, May, & Co.

The B, C, D, and E grades, containing 7½, 5, 2½, and 1¼ per cent aluminium respectively, decrease in tensile strength from about 65,000 per sq. inch in B to 25,000 lbs. in E grade. The transverse and torsional strength, elastic limit, and resistance to compression decreasing as the aluminium is lowered; elongation increasing in the same proportion. The E grade metal will stretch nearly two-thirds of its length before rupture, which exceeds that of pure copper by about 100 per cent. A piece of C grade wire can be twisted through several hundred turns before breaking. A rolled bar of C grade (5 per cent), tested at the Phœnix Works, Rohort, Germany, gave—

Tensile strength .. .. 82,880 lbs. to sq. inch—37 tons.
Elongation .. .. .. 60 per cent.

Average strength in castings:—

Grade.	Tensile strength per sq. inch.	Elongation.
"A" special (11 p.c.) ..	90—100,000	0—8·0 p.c.
"A" bronze (10 ") ..	75—90,000	4—14 "
"B" " (7½ ") ..	55—65,000	20—40 "
"C" " (5-5½ ") ..	35—45,000	30—40 "
"D" " (2½ ") ..	30—35,000	40—50 "
"E" " (1¼ ") ..	25—30,000	40—55 "

All grades of this bronze under 11 per cent can be rolled, swedged, or drawn cold, and is the only bronze that is not "hot-short," and can be worked at a bright red heat as easily as wrought-iron. Under the hammer it can be drawn out to the fineness of a needle.

The rolling of sheets, rods, bars, and wire is done at bright heat, only the finishing done cold. Rolling or working this metal in any way makes it stronger and tougher. A "rolled" rod, "B" grade, tested at the Otis Iron and Steel Works, Cleveland, Ohio, showed tensile strength 83,000 lbs. to the sq. inch, with 39 per cent elongation before breaking. In the casting this metal had but 60—65,000 lbs. tensile strength with 20 per cent elongation.

The fracture of the special and "A" grades exhibit a crystalline structure; the lower grades are extremely fibrous.

The beautiful colour and power of resisting corrosive influences make aluminium bronze valuable in art metal work.

In the church of St. Germain, Paris, are twelve beautiful candlesticks, six feet high, and a crucifix four to five

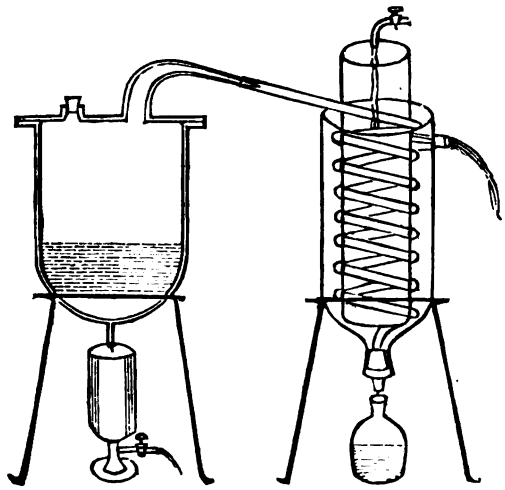
feet in height, made of 5 per cent aluminium bronze—these have been in position over twenty years, and their colour is still perfect. In Philadelphia the statue of Wm. Penn, intended to surmount the dome of the new city hall, will be cast in aluminium bronze.

(To be continued).

ESTIMATION OF SILICA AND ANALYSIS OF SILICEOUS MATERIALS.

By GEORGE CRAIG.

The process in most general use for estimating silica is, I believe, to fuse with alkaline carbonates and decompose with HCl, with subsequent evaporation to dryness. From many experiments it seems that no more than 97·5 per cent of the total silica can be obtained when pure silica or siliceous matter is subjected to the treatment just mentioned. The subsequent estimation of the silica remaining in solutions is a very tedious operation, and unsatisfactory after all. By decomposing with H_2SO_4 this difficulty may be overcome, and all the silica obtained insoluble; but the large amount of alkaline salts, introduced for purposes of fusion, necessitates the re-solution and re-precipitation of the Al_2O_3, MnO_2, CaO, and MgO



precipitates obtained in the filtrate from the silica. Thereby ammonia and soda salts increase to such an extent that their solvent action on the precipitates and on the operation-vessels becomes considerable. So much is this the case that, by evaporating the filtrate from the MgO precipitate to dryness in a platinum basin, expelling all volatile salts, dissolving in water, and rendering alkaline with Na_2CO_3, a considerable precipitate is obtained, consisting of SiO_2, Al_2O_3, CaO, MgO, and P_2O_5. The unreliability of figures obtained under such circumstances caused me long ago to discard the fusion process, and in all cases to expel SiO_2 with HF and H_2SO_4, and estimate the other ingredients in the residue. As may be imagined, careful analyses of the same material by both processes, using glass and porcelain vessels, show considerable differences, and there can be no doubt which is the more correct. I have no doubt this process is used by a great number of chemists; but the publication, ever and anon, of analyses performed by fusion processes convinces me that the errors inherent to the one and the accuracy and rapidity of the other are not sufficiently known—hence this communication.

For the expulsion of the silica, sufficiently pure H_2SO_4 may be had from the dealers, which is best employed after dilution with an equal vol. of water.

Commercial HF requires to be re-distilled, and for this purpose is introduced into a 10 or 12 ozs. capacity leaden retort and the vapours passed through a coil of red india-rubber tubing (¼ in. bore) immersed in water. The tubing is best wound spirally about a piece of 2 in. diameter glass tube, which serves to support it, and, at the same time, to introduce the cold feed-water at the bottom of the containing vessel, which is the same as that supplied with the ordinary spiral glass condensers. The arrangement is shown in the accompanying sketch. The first portion of the HF distilled is rejected, or it may be re-distilled, as it is contaminated with impurities derived from the rubber, but after a little the distillate leaves no residue on evaporation.

A blank experiment should be performed by evaporating 100 grains of the H_2SO_4 to dryness with a little HF, and ascertaining the weight and nature of the ignited residue, so that it may be allowed for.

Process.—20 or 25 grains of the very finely ground material are placed in a deep platinum crucible and H_2SO_4 added in quantity more than sufficient to form sulphates with all the bases present. About 50 grains bulk of the pure HF is added, and, after mixing well by shaking gently, the crucible is kept over the lowest flame of an Argand until almost dry. One treatment with HF is usually sufficient to expel all the SiO_2, but for surety I always repeat the operation, and heat more strongly at the finish *until H_2SO_4 is evolved.*

This is the only point requiring special attention, for fluorides are formed, and no amount of heating with excess of H_2SO_4 decomposes them unless the heating is continued until H_2SO_4 itself is evolved. By neglecting this no end of trouble may be incurred thereafter by the precipitation of fluorides, and totally erroneous results will be obtained. As the white fumes, towards the finish, may easily be mistaken for H_2SO_4, I invariably test the fumes by holding a gloss rod moistened with dilute NH_4HO in them and dipping it into a test-tube containing dilute acidified $BaCl_2$; no precipitate is given until H_2SO_4 is present. When the crucible has become cold HCl is added and gentle heat applied, until all is dissolved. By covering the crucible with a platinum capsule filled with cold water, which can be withdrawn and renewed by means of a pipette when it becomes warm, condensation of the HCl vapours takes place, all loss by spirting is avoided, and solution hastened. When thoroughly dissolved the acid solution is washed into a beaker, diluted, and the alumina and other ingredients estimated as usual. When precipitating the Al_2O_3, &c., I prefer to colour the solution with litmus, add NH_4HO till just blue, and filter whenever the precipitate settles, thus avoiding all chance of error from the solution of the ingredients of the glass by long boiling. The precipitate is washed with water containing a little NH_4NO_3, until the filtrate is free from SO_3, but, as it may still contain some basic sulphate, it may be re-dissolved. This, however, is unnecessary, as, after ignition for some time at a high temperature over a blowpipe, the precipitate never contains more than immaterial traces of SO_3. This precipitate contains all the Al_2O_3, TiO_2, Fe_2O_3, P_2O_5, and a little Mn_3O_4. The bulk of the manganese, practically all when not much is present, remains in the filtrate, and is precipitated by NH_4HO and bromine-water. CaO and MgO are estimated in the filtrate.

Alkali is estimated by Lawrence Smith's process. By weighing as sulphate, estimating, and deducting the SO_3, the amount of $(KNa)_2O$ is obtained more rapidly than otherwise, and, if required, the proportion of K_2O and Na_2O can be obtained from these data by calculation.

Lugar Iron Works, Cumnock, N.B.

On Horse-Fat.—The weight of horse-fat remains unchanged for about four weeks. In the course of two years the increase due to the absorption of oxygen and the formation of free acids amounts to 3·495 per cent.—*Zeit. Anal. Chem.*, Vol. xxviii., Part 4, 1889.

A SIMPLE SUBSTITUTE FOR KIPP'S APPARATUS.

By EUSTACE THOMPSON.

The accompanying sketch represents a simple contrivance for supplying a continuous and steady stream of carbonic acid. The flask, with a capacity for 500 to 600 c.c., contains hydrochloric acid. The bottle, fitted with a tap-tube, contains chips of marble. They are connected by a tube in the form of a syphon reaching to the bottom of each. The flask is also provided with a tube similar to the shorter tube of a wash-bottle, and for a similar service; it has been represented in its present position for convenience in drawing, but should be turned through 90° towards the reader for convenience in operation. When the evolution of gas is required the tap-tube is opened and the pressure within the flask increased just sufficiently to fill the syphon-tube with acid. Directly acid enters the bottle gas is evolved and more acid flows over. If it is desired to stop the evolution the tap-tube is closed, and the pressure exerted by the gas confined in the bottle rapidly drives the acid into the flask again and empties the syphon. If a steady and continuous stream

of gas is required the opening of the tap-tube can be regulated, with a little trouble, in such a manner that, when once the syphon-tube has been filled with acid, only a small quantity will run into the bottle, because the pressure of the gas, being allowed only limited freedom in egress, is sufficient to prevent an excessive quantity of acid from flowing in. But, as the hydrochloric acid in the bottle becomes saturated with calcium carbonate, its action becomes less vigorous, and the pressure of gas would be diminished but for the fact that additional acid, thus permitted to flow over very gradually, is just sufficient to keep it at the same height.

In the same apparatus the marble may be replaced with zinc or with sulphide of iron for the preparation of hydrogen or of sulphuretted hydrogen respectively. It is, in fact, a simple substitute for Kipp's apparatus. One advantage, not altogether inconsiderable, which gives it a preference to the latter, is, that it requires a far smaller quantity of acid; that which has not dissolved calcium, iron, or zinc chloride remaining in the flask till required, does not mix readily with the portion already saturated, and, when all is saturated, it is very easily replaced by a fresh quantity.

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Bradford Technical College.

EXPERIMENTAL RESEARCHES IN THE REDUCTION OF THE DIFFICULTLY REDUCIBLE METALS.

By A. J. ROGERS.

Aluminium (Al) was probably first obtained by Woehler n 1827 by treating the chloride with the metal potassium, (iK).

Sir Humphry Davy obtained sodium (Na) and potassium (K) in 1808 by the electrolysis of the fused hydroxides of those metals.

He tried to obtain Al by the same method from alumina, but was unsuccessful. Bunsen first obtained minute quantities of the metal by the electrolysis of the fused double chloride of aluminium and sodium (Al_3Cl_62NaCl) in 1854. In the same year, Henry Ste.-Claire Deville first prepared the pure metal in sufficient quantity to be able to study its properties. His process was by the reducing action of Na upon Al_2Cl_62NaCl, using about one-third of cryolite as a flux.

The Deville process has remained, with but slight changes in detail, as the only practical process for the extraction of pure Al. Deville first established a small plant at Javel, France, but later united with Debray, Morin, and Rosseau Brothers. Still later, Merle and Usiglia, in Salindres, gave Deville's process the high perfection that it has to-day. By that process the largest item of cost is the sodium used. In 1852 Na sold at two hundred dollars a pound, but in 1862, by improvements in the process of manufacture, it had been reduced to a dollar and a half a pound. Al_2Cl_6 and Al_2Cl_62NaCl are very hygroscopic, and, when heated in presence of air moisture, hydrochloric acid, and alumina are formed in considerable quantity. During the reduction with Na it is claimed that alumina would form upon the surface of the minute globules of aluminium and thus prevent cohesion between them. Cryolite was used as a flux to assist in removing this oxide. Prof. H. Rose first used cryolite (the double fluoride of sodium and aluminium, Al_2F_66NaF,) as a source of Al. He heated cryolite with Na in an iron crucible, using KCl as a flux, and stirring with an iron rod. His metal, of course, always contained some iron. Rose never obtained more than 80 per cent of the theoretical amount of Al in the cryolite, and many times not more than 33 per cent.

Basset affirmed that all metals will decompose Al_2Cl_6 or Al_2Cl_62NaCl which form chlorides that are more easily liquefied or vaporised than these salts. Hence arsenic (As), antimony (Sb), mercury (Hg), and zinc (Zn) would act as reducing agents of Al. Zinc would seem to be the best from its cheapness and the greater ease of separating from its alloy of Al by distillation of the zinc. According to Basset, the operation consists in heating 3 parts of Al_2Cl_62NaCl with 2 parts of zinc. By stirring, the chloride mass gets denser and finally solid, while the resulting Al alloy remains liquid. This salt mass and alloy are heated to a strong red heat for an hour or more; the molten mass is then stirred with an iron rod, and the salt poured off after the solidifying of the metal. An alloy is obtained consisting of equal equivalents of Al and Zn. Basset's process was recommended by Wedding and others. Specht, in 1860, decomposed Al_2Cl_6 by the use of Zn, and recommended it as the best process in practice.

Dullo states that there is no difficulty in reducing the double chloride with Zn, but it is not as easy as with Na, and the loss of Zn is considerable, and the high temperature required also burns a great deal of Al. My own experience is that the reduction is very incomplete, and only a very small percentage of the Al contained in the salt can be obtained. The Zn process has been more recently experimented upon by F. J. Seymour. He claims to use 100 parts of the Zn ore, 50 parts of kaolin, 125 parts of carbonaceous matter, 15 parts of pearl ash, and 10

parts of NaCl. It is not probable that much Al would be obtained by this process; certainly not pure Al. Petitjean decomposes sulphide of Al by heating in a crucible, through the bottom of which a stream of marsh-gas passes. He also claims to have effected the reduction by mixing the sulphide of Al with iron-filings and igniting. Cumenge ignited sulphide of Al with clay or Al sulphate free from water. Corbelli, in Florence, took 100 parts of clay with 600 parts of H_2SO_4 or concentrated HCl and gradually heated to 500°. This mass is mixed with 200 parts of KCN, 150 NaCl, and heated to a white heat. Deville was unable to obtain Al by this process. Knowles reduced the chloride by KCN, Fleury is said to have produced Al from clay mixed with gas-tar, rosin, petroleum, or similar substances. This was made into a dough and formed into balls, which, after drying, were heated in a tube at a cherry-red heat with marsh-gas under 20 to 30 pounds pressure. The reduced Al, in a fine powder, was melted with Zn, and the Zn afterwards distilled. None of these processes, except Deville's sodium process, have attained any prominence, and it would seem quite impossible to be able practically to reduce Al from its salts or ores by the use of ordinary reducing agents, including the common cheaper metals. Some years ago I commenced a study of some of the problems involved in the production of the difficultly reducible metals from their fused salt by electrolysis. Some results of an investigation of the alkali metals were given in a paper before the Physical Section of the American Association for the Advancement of Science, at its meeting in Ann Arbor in 1885. The principal points stated and conclusions reached in that paper I give in the following summary :—

I had observed, according to J. J. Thomson, that the heat of chemical union of one pound (or kilogrm.) of Na with Cl to form NaCl is 4247 centigrade units; while that of carbon (C) with oxygen (O) is about 8000 units. Hence, in the combustion of one pound of C heat enough is obtained to reduce nearly two pounds of Na from NaCl if the heat energy could be utilised without loss. But no purely chemical method has even yet been suggested by which this kinetic heat energy of the coal, or C, can be transformed without loss into potential energy of separation of the Na and Cl in NaCl. If electrical energy can be applied without loss to produce the separation of NaCl into its constituent elements, we can easily compute the amount of coal used in a steam-engine to give the necessary amount of electric energy in the dynamo machine to produce a given amount of Na. Thus one mechanical horse-power per hour is equivalent to about 1425 heat units (pound degrees centigrade), and therefore this energy transformed without loss into electrical energy, and this electrical energy again into chemical work in decomposing NaCl, would give us (4247 divided into 1425) nearly one-third of a pound of Na per horse-power per hour, or 8 pounds a day of twenty-four hours. In practice, one mechanical horse-power applied to the dynamo machine generally yields not more than 80 to 90 per cent of one electrical horse-power. Thus, if there were no transfer resistance in the passage of the electric current through the molten NaCl electrolyte, but all the energy of the current were changed into chemical work, from 6 to 7 pounds of sodium would be set free at the negative electrode in twenty-four hours. Again, the electro-chemical equivalent of Na is 0·000238 grm., *i.e.*, with one ampère of current that amount of Na should be deposited at the negative electrode in one second of time, 0·8568 grm. would be deposited in one hour, or 20·56 grms. in twenty-four hours. Hence, 178 ampères would be required to deposit 8 pounds of Na in twenty-four hours. Since there are 746 watts to one electrical horse-power a voltage of (746 divided by 178) 4·2 would be necessary.

F. Exner (*Wiedemann's Annalen Band*, vi., Seite 353) gives the potential difference of Na and Cl at 2·06 to 2·08 Daniells, which would indicate, if correct, under our given conditions, a deposit of nearly twice 8 pounds in twenty-four hours. In a similar manner I computed what should be the theoretical value for the amount of deposit of other difficultly reducible metals in the electrolysis of their fused salts. It seems probable that the electrolysis of NaCl and allied salts can never be carried on successfully in any aqueous or other ordinary solutions, on account of the secondary products that are formed by the action of the liberated ions. So it would seem that the salt must be rendered liquid by fusion. The temperature of fusion may be lowered considerably in many salts by the presence of other salts, *e.g.*, NaCl melts at 200° below its ordinary melting temperature (776° C., according to Carnelley) in the presence of a small amount of $CaCl_2$, and its temperature is considerably lowered by the presence of a small proportion of KCl. In my experimental work various kinds and forms of crucibles and electrodes were used without my being able to obtain very much pure metal. But my intent was mainly to get some quantitative results as to the amount of deposition of metal at the cathode. For measuring strength of current, water, silver, and copper voltameters, of my own construction, were used, as also a tangent galvanometer, whose reduction factor had been carefully determined. The following results, among many others, were obtained, at the time using a Grove battery, for electrical power, a Battersea crucible for containing the NaCl, a carbon anode, and an iron cathode terminating in a tube of lime placed in the melted salt. As soon as metallic Na was seen to escape and burn at the surface of the liquid, the current was stopped, liquid cooled, crucible broken, and the amount of Na determined by a standard acid solution. Some of the Na was oxidised, while a considerable amount would be found in the tube in the pure metallic state.

Exp.	Ampères.	Time in seconds.	Observed amount Na. Grm.	Theoretical amount Na. Grm.
1.	3·2	90	0·04	0·066
2.	2·5	480	0·14	0·286
3.	2·8	360	0·16	0·24
4.	2·8	300	0·17	0·20
5.	3·5	420	0·2+	0·36
6.	2·0	480	0·13	0·22

The loss can be accounted for from the escape of some of the volatilised Na into the air and from diffusion and re-composition with the liberated chlorine. The resistance, measured by the method of substitution, varied from 1 to 1·5 ohms, with an average of about 1·3. Four large chromic acid cells were used in series in much of the work. It thus seemed that, with suitable apparatus, from 5 to 6 pounds of Na could be produced in twenty-four hours to one electrical horse-power. Thus, if there were no practical difficulties in the construction of crucibles and other apparatus involved, nor in working continuously on a large scale with a raw material so cheap and pure as NaCl, the metal could be obtained at small cost, and could be applied to the reduction of other difficultly reducible metals, including that very valuable metal Al. Various forms of crucibles were used and attempts made to distil the metal when formed at the negative electrode. Na volatilises at near 900° C., and when obtained from the electrolysis of NaCl, carries with it a large amount of vapour of NaCl, so that distillation is attended with some difficulties. Small specks of Al were also obtained by direct electrolysis of Al_2Cl_62NaCl, and of Al_2F_66NaF, but only a small percentage of the theoretical yield could be obtained.

Since the preparation of the paper of which the preceding is an outline, I have given attention more particularly to the direct electrolysis of salts of Al, using different salts of the metal with different fluxes, and different forms and materials for crucibles and electrodes. Some of the many points to consider in attempting to obtain Al by the direct electrolysis of its salts are the following :—

1. Cheapness of the salt or material used.

2. A salt whose melting-point is above the melting-point of the Al, and boiling-point below that of Al.

3. That will to the least extent attack the material of the crucible and electrodes.

4. Which offers the least transfer resistance.

5. Which does not dissolve the metal when once liberated at the cathode.

6. That does not facilitate diffusion of the ions and thus permit their re-uniting.

The salts that have been found in practice necessary to use are the anhydrous chlorides and fluorides of Al; more commonly the double salts with sodium. The double chlorides, as given in Hofmann's reports for 1872, cost at the factory in Salindres, France, 22 cents per pound, which would make its cost for a pound of Al 2·20 dols. The Webster-Castner works, at Oldbury, near Birmingham, now have facilities for manufacturing the double chloride in much larger quantities than heretofore, and have undoubtedly made improvements in minor details; but the general process remains the same as it was in 1872, and no great reduction in cost can be expected. The double chloride can be made quite free from silicon (Si), but always contains some iron (Fe). Cryolite is necessarily used as a flux when the double chloride is reduced by Na. The action of the cryolite has been explained as dissolving the thin coating of oxide that forms around the reduced particles of Al.

It may be, however, that the action of the cryolite is not that of a solvent of the oxide of the metal simply, but that it assists in decreasing the surface tension of the minute globules of metal, or otherwise mechanically causing them to cohere. The native double fluoride (cryolite) can be obtained much cheaper than the double chloride.

From the Government reports of mining and mineral statistics, the amount of cryolite imported into the United States is from 5000 to 8000 tons per year, at a cost of about 15·00 dols. per ton. This cost, the Pennsylvania Salt Co. (who control the cryolite business in this country), have told me is incorrect and too low.

They sell what they call pure cryolite at 125 dols. per ton, or 6·5 cents per pound. This would make the cost of an amount sufficient for one pound of Al 65 cents, supposing the yield of Al is 10 per cent of the salt (theoretically nearly 13 per cent). This so-called pure cryolite from the Pennsylvania Salt Co. contains, I find, 2 per cent of silica and 1 per cent of Fe. I am confident that the artificial fluoride can be prepared at half the cost and of much greater purity than the natural cryolite.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 1, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. T. A. Garrett was elected a Member of the Society.

The following communications were read:—

"*On a New Electric Radiation-Meter.*" By Mr. W. G. Gregory.

The meter consists of a long fine platinum wire attached to a delicate magnifying spring of the Ayrton and Perry type, and stretched within a compound tube of glass and brass. At the junction between the wire and spring a small mirror is fixed. When the tube is placed parallel to a Hertz's oscillator in action, the mirror is turned in a direction indicating an extension of the wire. The arrangement is so sensitive that an elongation of 1·200,000th of an m.m. can be detected. This apparent extension is such as would correspond to a change of temperature of 0·003° C. By its aid the author has roughly verified Hertz's statements that at considerable distances the intensity of radiation varies as the inverse distance but before he can proceed further it is necessary to greatly increase the sensibility of the apparatus; and with a view of obtaining some suggestions in this direction he exhibited it before the Society.

Prof. Perry asked if the E.M.F. required to produce the observed results had been calculated; he also believed that the sensibility might be increased by using copper instead of platinum, and replacing the spring by a twisted strip.

Mr. Blakesley enquired whether the effect of increasing the capacity of the ends of the wire had been tried.

Mr. Boys said if the observed effect was due to rise of temperature he would like to see it measured thermally. He also thought the effect might be due to extension caused by rapid electric oscillations in some such way as the elongation of an iron bar caused by magnetisation.

In answer to this Prof. S. P. Thompson said the matter had already been investigated experimentally, but with negative results.

Prof. Herschel suggested the use of a compound spring, such as are used in Breguet's metallic thermometers.

In reply Mr. Gregory said he had estimated the E.M.F. by observing that a Lechlanchè cell through 50 ohms produced about the same result. No improvement in sensitiveness was obtained by using copper wire or by increasing its capacity, and attempts to measure the rise of temperature by an air thermometer had been given up as hopeless.

The President, in thanking the author for his paper, congratulated him on the ingenuity and courage displayed in producing an apparatus to measure such microscopic quantities as are here involved.

"*On a Method of Driving Tuning-Forks Electrically.*" By Mr. Gregory.

In order to give the impulses about the middle of the stroke, the fork is arranged to make and break the primary circuit of a small transformer, the secondary circuit of which is completed through the electro-magnet actuating the fork. The prongs of the fork are magnetised and receive two impulses in each period.

Another device was suggested where the prongs respectively operate contacts which successively charge and discharge a condenser through the coils of the actuating magnet.

Prof. S. P. Thompson said the methods, if perfect, would be of great service, and suggested that a fork so driven be tested optically by comparison with a freely vibrating one. He regarded the mercury contacts used as objectionable, for their capillarity and adhesion would probably cause the impulses to lag behind the appointed epochs.

Prof. M'Leod remarked that Lissajou's figures gave a satisfactory method of testing the constancy of period, and could be readily observed without using lenses, and, in reference to liquid condensers suggested by the author for his second device, said that platinum plates in sulphuric acid were found to disintegrate when used for this purpose. He thought lead plates would prove suitable.

Prof. Jones, who read a paper on a similar subject in March last, said he now used bowed forks with which to synchonise the speed of the disc there described, and the frequency is determined by causing the disc to complete the circuit of his Morse receiver once each revolution.

"*On a Physical Basis for the Theory of Errors.*" By Mr. C. V. Burton, D.Sc.

After pointing out that the law of error for any particular measurement depends on the nature of the conditions governing such measurement, the author considers several simple cases and deduces their curves of error. A kinematic method of combining two or more independent errors, each following known laws, is then described and applied, and the general formula obtained leads to

Laplace's law of error in the case of an infinite number of similar errors.

Referring to *Most Advantageous Combinations of Measures*, it is shown that the method of least squares is only a particular solution of the general equation, and is derived by assuming the individual errors to conform to Laplace's law.

Subjective Errors are next considered, and in conclusion the author says that "the law of error in a set of observations depends on the nature of each special case, and what may be called the probable law of error is determined by our knowledge of the conditions. The combination of three or more sources of error of comparable importance gives, in general, a law not seriously differing from that of Laplace, so that the method of least squares will be practically the most advantageous, except where a single source of error with a very different law is predominant above all the rest."

"*A Note on the Behaviour of Twisted Strips*," by Prof. J. Perry, F.R.S., had been prematurely announced by mistake, and he accordingly gave only a brief outline of the paper.

In a previous communication Prof. Ayrton and the author enunciated a working hypothesis, in which the strips were imagined to be split up into pairs of filaments, each pair acting as a bifilar suspension. The resulting formula for the rotation produced by a given load did not agree with experiment, and quite recently the author had recognised why the formula was incorrect. The bifilar law they had assumed was only true for small twists, but he now saw another method of treatment by which he hoped to verify the formula derived from experiment before the next meeting.

Prof. Fitzgerald reminded Prof. Perry of a method of attacking the problem suggested by the speaker some time ago, in which each filament was supposed to be wrapped round a smooth cylinder, and said that on working it out the formula was found to be very complicated.

Mr. Trotter thought the pairs of strips might be regarded as twisted ladders, and

Mr. Gregory said this suggestion reduced the problem to a series of bifilar suspensions, which had already been worked out.

"*On Electrifications due to Contact of Gases and Liquids*." By Mr. J. Enright.

For some time past the author has been studying the electrical phenomena attending solution by connecting an insulated vessel in which the solution takes place with an electrometer. As a general rule, no effect is observed if nothing leaves the vessel, but when gases are produced and allowed to escape the vessel becomes charged with + or − electricity, depending on the nature of the liquid from which the gas passes into the air. As an example, when zinc is placed in hydrochloric acid the deflection of the electrometer is in one direction whilst the liquid is chiefly acid, but decreases and reverses as more and more zinc chloride is produced. From such observations the author hopes to obtain some information relating to atomic changes.

Owing to the lateness of the hour the latter portion of the paper and the discussion on it were postponed until next meeting.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 4, 1889.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Thomas Browning, C.B.; Latimer Clark, F.R.S., M.Inst.C.E.; Charles Pitfield Mitchell, M.R.C.S.; Maurice Powell, M.A.; and Delisle Powles.

Edward Pollock was elected a Manager of the Royal Institution in the room of Sir James Crichton-Browne, M.D., resigned; and James Edmunds, M.D., F.C.S., was elected a Visitor in the room of Edward Pollock, resigned.

The Special Thanks of the Members were returned to Professor Dewar, F.R.S., for his valuable present of a Portrait of the late Mr. Henry Pollock.

The Special Thanks of the Members were returned to the Rev. John Macnaught, M.R.I., for his second donation of £50 for improvements in the Building.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Laundry Management: a Handbook for Use in Private and Public Laundries; including Descriptive Accounts of Modern Machinery and Appliances for Laundry Work. By The Editor of *The Laundry Journal*. With numerous Illustrations. London: Crosby Lockwood and Son.

The day of small things is over, no less decidedly in the industrial arts than in States. Everything, to stand its ground against constant competition, must be conducted on the large scale. Articles which, within the memory of persons now living, were made in the back shops of the vendors, are now prepared on a vast scale in extensive specially constructed buildings with the aid of steam-power. The laundry was, till lately, an outhouse in country seats, a room in dwellings of humbler pretensions, serving also as the scullery, or perhaps the cottage of some industrious woman reduced to "take in washing."

Now, washing, in the neighbourhood of our large cities at least, has become a special business in which considerable capital is invested, and which is no longer carried on by rule of thumb.

The work before us, compiled by the Editor of the *Laundry Journal*,—a paper whose very existence is significant of the change which has taken place—seems to us to cover the whole field. It begins with a chapter on sorting and marking linen. Under this head we find a caution against the corrosive action of many marking-inks.

Next follows the important subject of disinfection. It is well known that many persons, who have small conveniences for washing and drying at home, yet prefer to have the house filled, weekly or fortnightly, with clouds of steam rather than run the risk of their clothing coming in contact with linen from a house where small-pox, diphtheria, or scarlet fever may be raging. The author is fully alive to the difference between true disinfectants and mere deodorisers, or maskers of evil smells.

Condy's fluid the author considers rightly objectionable, on account of its colour and the stains it leaves upon textile fabrics. He seems to be of opinion that Californian borax contains more boracic acid than that from any other source. This is an error; genuine borax, wherever it has been manufactured, and whatever may be its original source, contains one and the same proportion of boracic acid. He prefers, however, disinfection by means of hot air or steam, giving the precaution that the latter will injure many colours.

Water is the next question. As a matter of course, he condems hard waters as injurious, in the long run, to the goods washed, and as distinctly uneconomical. He recommends the Clark process, which is worked with such success on the water-supplies of Canterbury, Aylesbury, and Tring.

The caution that salts and soaps of soda should never be brought in contact with woollen tissues, now so thoroughly understood by wool-dyers, is not here given.

The question of adulterated soaps is discussed at some length. This is an evil which the public has brought upon itself by its rage for ostensible cheapness. There is, however, abundance of genuine honest soap in the market; the qualities most advertised being, as a rule, most to be suspected.

Soap-powders and soap-substitutes the author views with suspicion, and chloride of lime, he thinks, had much better be kept out of the laundry altogether. It is anything but pleasant to sleep between sheets which have been saturated with hypochlorites, troubling your rest with visions of St. Helens and Widnes. He denounces warmly, but justifiably, laundries which do a "cutting" trade, pay starvation wages, and make use of corrosive chemicals.

In the chapter on "blueing," the author says that ultramarine, "properly manufactured, is easily soluble"; a strange assertion.

The chapter on cleaning, renovating, and dyeing feathers, gloves, &c., seems rather out of place in a laundry handbook. There is also a section on carpet-beating open to the same objection.

Viewed as a whole the work must be pronounced useful to the trade, and beneficial to the the public, if its lessons are carried out.

Practical Photometry: a Guide to the Study of the Measurement of Light. By W. Jos. Dibdin, F.I.C., F.C.S., &c. London: Walter King, Office of *Journal of Gas Lighting*.

The art of photometry has latterly assumed great and increasing importance, and it is not too much to say that in the practice of this art Mr. Dibdin has come to the front in a very useful manner. Hitherto, we believe, there has not existed any guide-book to which the photometist might refer in novel and difficult cases. Such cases have of late become more frequent in consequence of the introduction of the electric light, and of burners which send down their rays at all angles. Under such circumstances, the work before us will generally point out the expedient to be adopted.

Mr. Dibdin begins with the history of photometry, which may, in reality, be said to have commenced with the felt necessity of keeping a check on "keen questioning directors." Says Mr. Dibdin:—"He (the gas maker) undertakes to supply a certain article for a certain price, and he can no more be expected to exceed that bargain than can the family butcher be asked to add an odd ounce or two to every pound of beef that he sells." We never heard of any person simple enough to entertain such expectations. But both gas maker and butcher, unless sharply watched, will fall below their bargain, and the gas maker being not, like the butcher, liable to competition needs a very close inspection. Why, otherwise, have gas examiners at all?

The mean value of the Carcel lamp, used as the standard in France, is given as 9·5 English normal candles. At the recent Congress of Electricians sitting in Paris it was recommended that our candle should be reduced in value so as to be exactly 0·1 Carcel. But if, as the author recommends, and as we certainly think it desirable, the pentane air-gas of Mr. A. G. Vernon Harcourt is adopted as the legal standard of reference, we need not trouble ourselves about any modification of the candle.

The next chapter treats of the principles of photometry. Here we find especial attention called to the influence of burners upon the results. At present, thanks to the legislature, the photometrist, before beginning to test, has to select a burner prescribed for the particular quality of gas. This system Mr. Dibdin very rightly pronounces confusing, and recommends its abandonment.

Much of the chapter is taken up with an abstract of an important paper read by Messrs. Heisch and Hartley before the Gas Institute in 1884.

In Chapter III. we find a discussion of "Horizontal Photometers." The author drily remarks that:—"The traditional way to make a 'new' photometer is to alter the wooden casing as much as possible and then to call this outcome of the cabinet maker's art a new photometer."

The form of the instrument here described, and mostly figured, are the King's, the Lethel, the Canadian, Keats's candle balance, the closed Evans, the open Evans, the Imperial, the Harcourt's Table, and the Portable.

We next come to the so-called radial photometers, which determine not merely the illuminating power of the rays falling horizontally, but of those falling at all angles from the horizontal to the vertical. Here we have Hartley's "universal" photometer, the author's own instrument, the radial, Sugg's travelling photometer, and the Lolophotometer.

After the description of these instruments comes an account of the two forms of discs, the Bunsen and the Leeson. Mr. Dibdin considers that the former, a greased disc, is unsatisfactory for testing electric lights or recuperative gas-burners, and has therefore abandoned it in favour of the modified Leeson.

Under "Standards of Light" comes an account of the English sperm candle, the French Carcel lamp, and the German paraffin candle, each of which has its shortcomings.

Among the proposed substitutes, Violle's solidifying platinum is rejected as not practical, whilst the Harcourt system, referred to above, is proposed as the standard of the future.

The amyl-acetate lamp (Von Hefner-Altenecks) is open to objection on account of its dusky flame.

The chapter on "Colour Photometry," is, perhaps, of questionable relevance in a work dealing with the values of sources of light. It contains a notice of Lovibond's tintometer, an instrument likely to supersede the old colorimeter. Although it was first made known in a paper read before the Society of Dyers and Colourists, it does not seem to have come into extended use in the tinctorial arts.

Stellar photometry, which forms the subject of the final chapter, is exceedingly interesting, though to routine gas makers and gas examiners it will seem out of place and unpractical.

An appendix contains the notification of the gas referees for the summer of the current year, the times and modes of testing for illuminating power, and for impurities, the limits for sulphuretted hydrogen, for ammonia, and for sulphur-compounds other than with hydrogen. Then follow figure and description of Sugg's London Argand burner, the gas referee's street-lamp pressure guage, table showing correction of volume of gas at different temperatures and pressures, blank forms of examiner's reports, gas referee's cubic foot measure, revised regulations as to gas-measuring standards, apparatus for testing gas meters, gauges for connecting pipes and fittings, proposed Board of Trade standards for gas-meter connection pipes and fittings, weight of oil burned hourly in Carcel lamp, and tables for candle corrections, and for the illuminating power of sperm lamps.

Mr. Dibdin's work must be pronounced not merely useful, but essential to all persons who are engaged in manufacturing, selling, or checking gas, and no less to those concerned in the introduction of the electric light.

The Air inclosed in the Soil.—Th. Schlœsing, Jun.—The author's results verify the fact of the abundance of oxygen in the ground air. The sub-soil, also, is in general well supplied with this gas. Save in exceptional cases, it cannot be said to have a reducing atmosphere. The composition of the gases collected is not alike at all times. In sloping ground carbon dioxide is not abundant at the lowest points.—*Comptes Rendus*, Vol. cix., No. 16.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—As Herr Wollheim now does "not for one moment dispute that other sludges may be inoffensive, even when first drawn from the tank," he, in fact, concedes all that I could desire. Sewage precipitates, of any manurial value, do not require to be left exposed for weeks to rain and sunshine, as they can be readily turned to better account.—I am, &c.,

The Writer of the Report.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—I have read with extreme interest Dr. Bennett F. Davenport's article upon milk analysis, which appeared in the Chemical News (vol. lx., p. 213). I thoroughly agree with him in all that he has written concerning the estimation of the fat in milk; the process employed being termed by him a modified Wanklyn. I am in the habit of using platinum basins of 2½-inch diameter but having quite flat bottoms, and have no difficulty whatever in obtaining a very thin and evenly distributed skin of residue; the complete extraction of which, by means of petroleum ether, is easily accomplished. Petroleum ether, as mentioned by Dr. Davenport, having a great advantage over that of ether in not dissolving either lactic acid or lactose.

The process known as the "Adam's blotting-paper," and recommended by the Milk Committee of the Society of Public Analysts, is a process which is decidedly faulty, and that in three respects, and my reasons for saying so are as follows:—First, you cannot estimate directly both the fat and the solids not fat. Second, that the amount of fat obtained is in excess of that originally present in the milk, owing to an increase in weight due to rapid oxidation of the fat when in contact with cellulose, when spread over such a large surface, and also to a further oxidation which takes place when completing the drying of the extracted fats in the water-oven. Third, it cannot be used when the milk is not fresh, objections which are fatal to any milk process, and which, by unprejudiced persons, connot be gainsaid.

I used blotting-paper in milk analysis in 1882 (before Mr. Adams) and relinquished its use, owing to the last objection, and, finally, by a long series of experiments, satisfied myself as to the correctness of my second objection, and when coupling that with the first and third objection I have now no hesitation in rejecting it as faulty.

My opponents may say that the fat calculated from the sp. gr. and total solids agrees that found by Mr. Adams's process, but to that I reply we have already had examples of altering formulæ to suit the particular process employed.—I am, &c.,

William Johnstone.

City Central Laboratory,
13, Fish Street Hill, E.C., Nov. 4, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In an article on "Milk Analysis" in the Chemical News (vol. lx., p. 213) Dr. B. F. Davenport states that the fat can be *entirely* extracted from the dried residue of 5 grms. of milk if only this be in a flat-bottomed platinum dish of 2½ inches diameter. He uses four separate quantities of boiling benzine. Unluckily he gives no comparative analyses to show that the fat is *entirely* extracted

For years I used exactly the method described, sometimes with larger flat-bottomed dishes, and always with more numerous changes of benzine, boiled on the residue. The fat, however, was never entirely separated, nor even to within "one-tenth of a per cent." In a paper in the *Analyst*, February, 1889, he will see this method contrasted with more modern methods. In my experience there are only four methods that extract all the fat from a milk:—1st, Soxhlet's areometric method; 2nd, Soxhlet's tube with pumice, plaster-of-paris, kieslguhr or paper-coil (Adams); 3rd, the lactocrite; 4th, the Schmid method. This last was described in the Chemical News, vol. lx., p. 214.—I am, &c.,

A. W. Stokes, F.C.S., F.I.C.

Analytical Laboratory,
Vestry Hall, Harrow Road, W.,
November 4, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 16, October 14, 1889.

Reciprocal Displacements between the Halogens and Oxygen; the Hydrobromic and Hydriodic Acids.—M. Berthelot.—A thermo-chemical paper, not adapted for useful abstraction.

New Relations between the Sugars and the Furfuric Compounds; Constitution of Methyl-furfurol and Isodulcite.—M. Maquenne.—If isodulcite is distilled with four parts by weight of sulphuric acid, of sp. gr. 1·109 to 1·152, we obtain an aqueous liquid smelling strongly of furfurol, which precipitates slowly on the addition of ammonia, and gives with phenyl-hydrazine acetate an insoluble and non-crystalline hydrazone. This liquid, if fractionated, gives off first a little acetone and then a dense yellowish oil, which passes over entirely between 186°—187°. This oil consists of pure methylfurfurol, identical with that obtained on the distillation of sea-weeds, and consequently with that from wood-tar.

The Fermentation of Raffinose in presence of various Beer Yeasts.—D. Loiseau.—The author refers to matter contained in a "sealed paper" deposited with the Academy, March 5th, 1888, some of which is not yet ready for publication. Raffinose ferments completely in presence of beer-yeast, from a "bottom" fermentation, yielding theoretical quantities of alcohol and carbon dioxide. With yeast from a "top" fermentation the process is incomplete, only about one-third of the normal quantities of alcohol and carbon dioxide being obtained; whilst there remains in the fermented liquid a substance which reacts upon Fehling's liquid, which ferments completely with bottom yeast while resisting top yeast.

Observations on M. Guignet's Communication of September 30th.—MM. Vincent and Delachanal.—M. Guignet states that he has been able to extract well crystallised mannite from the cupric precipitate obtained from a decoction of sea-weed and from the juice of mountain-ash berries before the separation of the sorbite. The authors find that sorbite is completely precipitated by M. Guignet's reagent. The production of this precipitate does not warrant us in inferring the presence of mannite in the juice of mountain-ash berries, nor its separation from sorbite.

The Optical Analysis of Oils and Butter.—E. H. Amagat and Ferdinand Jean.—This paper will be inserted in full.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 4.

On the Possibility of Communicating the Bouquet of a Wine of High Quality to a Common Wine by Changing the Ferment.—A. Rommier.—It appears that the flavour of a wine depends less on the nature of the soil in which the vines have been grown than on the ferment employed. The wine-ferments, which have been hitherto supposed identical and which have received the name *Saccharomyces ellipsoideus*, are various, and communicate different qualities to the must in which they set up fermentation. The juice of the "chasselas" grapes of the South of France can, by a change of ferment, be made to yield high-class (*grands crus*) Burgundies.

Detection of Saccharine in Mixtures.—Introduce into a flask about 20 grms. of the substance in question with an equal volume of water, and shake it up. Add 5 drops of sulphuric acid, shake, and pour in a volume of ether equal to that of the mixture; shake very gently to prevent the formation of an emulsion. After settling draw off the ether by means of a decanting-tube, evaporate it to dryness, and taste the residue. If saccharine is present it will have an intensely sweet taste. The evaporation of the ether must, of course, be conducted in the absence of fire or flame.

Reactions of Furfurol and their Utilisation for the Detection of Certain Organic Compounds, Amylic Alcohol, Alkaloids, &c. — L. von Vdranzky. — The author has studied a great number of substances. Among those which give coloured reactions in presence of furfurol and sulphuric acid some are coloured in the same manner, whether treated with sulphuric acid alone or with this acid and furfurol. Other bodies are coloured only when both reagents are employed, or at least the colour which they give with sulphuric acid alone is not the same as that produced by the joint action of sulphuric acid and furfurol.

Colours Produced by Furfurol and Sulphuric Acid.

Acetacetic ether ..	Red.
Acetone	Light cherry red.
Aniline	Bright red.
Anthracene	Greenish, then red, then blue.
Anthraquinone	Light red.
Atropine	Light rose.
Borneol	Peach-blossom, then violet, then blue.
Brucine	Light violet.
Cholesterine	Bright red and then blue.
Cinchonine	Light rose.
Coumarine	Light violet.
Dimethylaniline ..	Light rose.
Cresol	Light red, then violet, and then blue.
Ethylenic glycol ..	Bright raspberry red.
Malic acid	Light rose.
Methylic alcohol ..	Light cherry red.
Morphine	Raspberry red, then bluish.
Naphthol α	Splendid violet.
Phenanthrene	Violet.
Phenol	Cherry red, then blue.
Phenylhydrazine ..	Cherry red.
Phloroglucine	Raspberry red.
Protocatechuic acid ..	Violet, turning blue.
Pyrogallol	Bright cherry, then violet.
Quinic acid	Light violet.
Salicylic acid	Light rose red.
Strychnine	Dirty violet.
Tyrosine	Faint rose red.
Vanillic acid	Light rose red.

The method of applying the reagents is as follows:—A particle of the substance, if solid, or a drop if liquid, is put in a test-tube with 1 c.c. of water or alcohol, a drop of furfurol water at ¼ per cent is added, and about 1 c.c. of strong sulphuric acid is carefully let run in down the side of the tube. The bottom of the tube is kept in a current of cold water so that the temperature may not exceed 50°. In some cases, besides the colouration mentioned above, there is observed the formation of a green band. Some of the coloured liquids present peculiarities if examined with the spectroscope. This is the case with naphthol α; if examined after agitation there is a narrow band, not well defined at equal distances, between D and E. After F the spectrum is obscured. With ethylenic glycol we see two very definite bands, a broader one at E and a narrower one at F.

MISCELLANEOUS.

The Cornish Uranium Mine.—It is gratifying to find that a continuous lode of uranium ore—unique in the world—has been met with in the parish of St. Stephen's, Cornwall, about 1½ miles distant from Grampound Road. The lode varies in width from 3 to 5 feet, and the uranium ore is not distributed in bunches or pockets, as is the case elsewhere, but is continuous throughout. This valuable metal, worth at present about £2400 per ton, occurs in the state of uranic phosphate, though hydrated uranous oxide is also to be met with. Samples of the ore seem to have yielded, on the average, 12 per cent of the pure metal, though some samples run up to 30 per cent. The advantageous feature of this deposit of uranium ore, in addition to its continuous character, is its freedom from arsenic and other ordinary impurities, which render the extraction and purification of the metal difficult and costly. Our readers are, of course, aware of the uses of uranium, in giving green and golden colours to glass, in the production of a fine black upon porcelain, and in photography. But if a large and regular supply is available it may be used in electro-plating, and in the formation of gold-coloured alloys with platinum and copper, the former of which is said to resist acids. This may open the door at once to honest and dishonest arts.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Calcined Caustic Lime.—A correspondent wishes to know where this can be obtained in large quantities.—T. H.

Analysis of Cocoa, &c.—Can any reader refer me to papers or books which would help me in the analysis of cocoa, chocolate, and other confectionery?—Analyst.

MEETINGS FOR THE WEEK.

Friday, Nov. 15.—Physical, 5. "On Electrification due to the Contact of Gases and Liquids," by J. Enwright. "On the Effect of Repeated Heating and Cooling on the Electrical Resistance and Temperature Coefficient of Annealed Iron," by H. Tomlinson, F.R.S. "Notes on Geometrical Optics, Part II," by Prof. S. P. Thompson, D.Sc.

FOR SALE. — The Chemical Gazette.
Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," Chemical News Office, Boy Court, Ludgate Hill London, E.C

TO BE SOLD, the Lancashire Manure Company's Works at Widnes, with Machinery and 4,420 square yards of Freehold Land.—Address, J. Hosking 16, Fenwick Street, Liverpool

THE CHEMICAL NEWS.

Vol. LX. No. 1564.

DIMIDIUM:

An Attempt to Represent the Chemical Elements by Physical Forms; with Models of the Elements, from Hydrogen to Nickel, constructed in accordance therewith.*

By Dr. ISAAC ASHE.

The author pointed out that when the combining weight of an element was divided by the number representing its combining power, or valency, as compared in both cases with hydrogen, the quotient in many cases presented the fraction one-half, instead of an integer number; and that in many other cases, particularly in the triad series, an integer quotient with unity for a remainder was to be obtained by doubling the combining weight before dividing.

Hence he inferred that an element having half the weight of hydrogen would be found to be the primordial element out of which the other elements were constructed. This hypothetic element he proposed to call dimidium. The number of atoms of dimidium which would go to form any given element would be double the number representing the combining weight of that element as compared with hydrogen. Dimidium itself might probably consist of a number of vortex rings—according to Sir W. Thomson's theory—placed one on the top of another, thus forming an elongated circular bar; a limit would be placed to the length of the bar so compacted, in consequence of a point being reached on each side of the centre, in a lengthwise direction, where the forces of attraction and repulsion between the rings balanced each other. Possibly the hollow tube thus formed might itself be filled with some still lower form of matter, out of which the vortex rings themselves might have been made, perhaps perfect spheres, to which Mr. Crookes's term "protyle" might be applied.

Assuming, then, the existence of this primordial linear element, and representing its atoms by small metallic bars of brass wire, the author showed that—taking in each case the number of bars indicated as above, by doubling the combining weight of each element—he had been able to construct a series of models of the chemical elements, in which their combining power, their positive or negative condition, and their modes of combination, were all expressed, as well as their combining weight. He further shewed that the forms brought out in these models corresponded with the crystalline forms known to belong to certain of these elements; and how the phenomenon of the expansion of water when freezing might be explained by reference to the form employed for the molecule of that compound, which was hexagonal in its general outline.

The forms adopted for the elements in these models were also shown to correspond with the arrangement of the elements in series by Newlands and Mendeleeff, elements belonging to the same series having corresponding forms.

The author suggested that simple geometrical forms, that is to say, the equilateral triangle and the square, were the combinations into which the primordial element would first have entered, and all the models were accordingly constructed out of these forms, along with the simple bar. Thus, the atom of hydrogen was constructed of two single bars placed side by side, and the molecule of four, and he suggested that these were probably separated in the gaseous condition, so as to form a hollow cube. There were other secondary forms constructed out of the triangles and squares, and the models of many of the elements were then constructed out of these secondary forms.

Lithium was formed of two squares and two triangles, or 14 pieces, its combining weight being 7. Carbon was formed by placing two pyramids base to base, each pyramid being formed of four equilateral triangles, in all 24 pieces, its combining number being 12. The crystalline forms, both of the diamond and of graphite, were shown to correspond with this, the former being made by placing a number of the carbon atoms together by their edges, and the latter by placing them in apposition by their triangular facets.

Silicon was formed by replacing each of these triangles by a group of seven, formed of two triangles united at their bases and separated at their vertices by a single bar component. This was shown to correspond with the crystalline forms of silicon.

Sodium and potassium were so constructed as to correspond with the form adopted for lithium, these being all members of the same series. Similarly, magnesium and calcium were so constructed as to correspond with beryllium, phosphorus and vanadium with nitrogen, sulphur with oxygen, chlorine with fluorine, &c.

Iron, and the group of tetrad elements analogous with it, were constructed out of a common base form consisting of 88 components, to which pairs of secondary forms, consisting of 20, 22, and 24 components respectively, were added to represent chromium, manganese, and iron respectively. The forms adopted for all these elements corresponded with that representing aluminium, so that the replacing of an atom of this latter element by one of any of the former in the alum compounds was shown to be in accordance with the theoretical forms assigned to these elements.

The author suggested that probably metals combined with non-metals by lateral interpenetration, a salient angle of the former corresponding with a re-entrant angle of the latter; but that two non-metals combined by superposition, corresponding angles being applied one to the other. The union of boron with nitrogen at a high temperature was shown, by reference to the models, to be an illustration of this view. The compounds of oxygen with nitrogen and with chlorine were also discussed, and a corresponding explanation of them suggested. What is known as the nascent condition of elementary atoms was explained as consisting in a sliding movement between two atoms which had been combined, so that one of these was removed gradually from the other, while a third gradually replaced it by a similar sliding movement, the atom so removed necessarily entering into combination with a fourth.

* Abstract of a Paper read before the British Association, Section B, Newcastle Meeting.

THE USE OF GLYCERIN IN PRESERVING SOLUTIONS OF SULPHURETTED HYDROGEN.

By ALFRED J. SHILTON, F.C.S.

A number of conflicting statements have been made as to the action of glycerin on a solution of sulphuretted hydrogen; I think it was Lepage who first recommended its use in the laboratory for this purpose, but it has since then been denied to have any preservative action whatever. Perhaps the following simple experiment will clear up the matter once for all:—

On November 6th I made up two white glass-stoppered bottles (*a*) and (*b*).

(*a*) Contained 50 c.c. saturated solution of sulphuretted hydrogen gas in water.

(*b*) Contained 50 c.c. of the same solution as in (*a*), but with 1 c.c. of glycerin in addition. The bottles were placed side by side on the laboratory shelf, and were left

until December 31st; they were then opened, and each of them found to smell strongly of the gas and to give a precipitate with lead acetate solution. They were re-closed, and not again examined until March 30th. When opened on that date the bottle (*a*) had entirely lost its odour, and gave no precipitate with a salt of lead, but the bottle (*b*), which contained the glycerin, had a strong odour, and gave a copious precipitate with lead acetate.

THE IODINE ABSORPTION OF ESSENTIAL OILS.

By R. A. CRIPPS, F.I.C.

Mr. Rowland Williams (Chemical News, vol. lx., p. 175) has drawn attention to the use of Hubl's iodine absorption test as applied to the examination of essential oils.

It is, however, somewhat unfortunate that Mr. Williams has apparently deviated from the lines laid down by Mr. R. H. Davies, whose paper on the same subject was published in the *Pharm. Journal*, [iii.], xix., p. 821; consequently his results differ widely from those obtained by Mr. Davies. The latter, in his paper, has shown that many essential oils act but slowly upon Hubl's reagent; it is therefore necessary to allow the digestion to be continued during a night. Mr. W. H. Snow has also shown the desirability of giving a longer time than two hours to the digestion; he finds that some oils require 40 hours, and even longer, for the completion of the reaction. This is, however, too long for practical use; it were better to adhere to Mr. Davies's plan of digesting during a night, but allowing a definite time, say eighteen hours, which is sufficiently long for the great majority of essential oils.

Temperature is another important factor in the determination of the iodine absorption of essential oils; at any rate, in those cases in which the reaction does not become completed in eighteen hours at the ordinary temperature, the difference between an ordinary summer and winter temperature would be sufficient to render the results untrustworthy. For the sake of comparison I append a Table of the results obtained by different observers with the most important oils.

I will not trespass further upon your space to make extended remarks upon the above Table; it is evident that the test is practically valueless unless performed under strictly concordant conditions, even then its indications will be of no value until a considerable number of samples of each essential oil have been reported upon.

A SPECIFIC GRAVITY BOTTLE FOR USE IN TROPICAL CLIMATES.

By C. J. H. WARDEN,
Chemical Examiner to Government, Bengal.

The specific gravity bottle, with a capillary fore-stopper, though commonly used in temperate climates, cannot be used in Bengal, for the following reasons:—In my laboratory, Calcutta, for a greater part of the year the temperature is usually between 80° and 95° F., and the air highly charged with moisture. Under such conditions, when a specific gravity bottle is filled with liquid, cooled to 15·5° C., and the capillary fore-stopper inserted, the bottle cannot be immediately weighed, because, owing to the extreme humidity of the air, water is condensed on the surface of the bottle far too quickly to admit of even very rapid weighings, and by the time the temperature of

Name of oil.	Barenthin.	Davies.	Snow.	Williams.
Almonds		None		
Aniseed	164·0	189·7	121 (40 hrs.)	185·9, 274·4
Bergamot	260·0	276·1	345 ,,	247·9, 283·7
Cajeput				70·85, 151·0
Caraway	265·0	*254·9	233 ,,	258·3, 463·2
Cassia		159·5		71·7, 75·1
Cedar				74·8, 78·5
Celery		*311·6		
Chamomile		*68·1, *72·1, 65·5		
Cinnamon	100·0	189·5		105, 128·1
Citron				320, 353·9, 359·66
Citronelle				186·3, 191·25
Clove (English)	270·0	349·5, 355·1, 362·5, 366·6	467 ,,	155·5, 179·8
Cubebs (English)		223·1, 226·0, 226·8		
Dill		*257·1		
Eucalyptus				61·7, 106·5, 110·6
Fennel	140·0	158·3		
Juniper	245·0	*337·3, 363·9†		236·1, 250·1, 273·5
Lavender (English)		265·5, 274·9, 273·9	286 ,,	230·4, 232·9, 248·6
,, (French)	170·0	262·7, 286·2, 294·5		198·6, 199·2, 237·2
,, (Spike)				287·9, 207·0
Lemon		328·3, 340·3, 345·3	343 ,,	320·16, 322·96
,,		348·9, 348·0, 345·6		
,,		355·1		
Nutmeg		*308·3, 321·5†		201·9, 206·25
Orange			362	341·7, 347·7
Pennyroyal		†188·9	152 ,,	85·9, 78·6
Peppermint (English)		49·6, 51·2, 57·7		36·85, 46·37
,, (American)		121·8, 132·2, 143·9 81·9	23, 84·7, 88·3 (6 hrs.) 24·5, 74·1, 73·6 (15 hrs.) 179, 109, 67, 71, 106, 105 (40 h.)	71·7, 53·1
,, (Jap.)		48·1, 43·5	64 (40 hrs.)	56·1, 37·1
Rosemary	185·0	†325		161·7, 142·4
Sandalwood (English)		226·6, 233·9		
Turpentine	300·0	377	397	

* English. † Foreign.

the liquid has reached that of the balance case it has necessarily expanded, and a large amount escaped through the capillary orifice in the stopper. In order to obviate this difficulty, 1884, I had ground on to the neck of the bottle a light glass cap, with a capillary orifice at the top, of sufficient capacity to hold 4 or 5 c.c. when using a 50 grm. bottle. The bottle is filled with the cooled liquid in the usual way, the capillary fore-stopper inserted, quickly wiped, and the glass cap fixed tightly on the neck. The bottle is then allowed to reach the temperature of the air, the expanded liquid forced out through the capillary orifice in the stopper being prevented from escaping by the cap, the capillary orifice in the top of the cap allowing the displaced air vent. Obviously it is very essential that the glass cap should be most accurately ground on to the neck of the bottle.

I ought, perhaps, to apologise for describing so simple an experiment, but, so far as I am aware, bottles modified on the plan I have detailed have not hitherto been procurable from instrument makers. Messrs. Edward Cetti, of Brooke Street, London, E.C., are now, however, prepared to supply capillary fore-stoppered specific gravity bottles with caps, for use in tropical climates.

Calcutt

AN IMPROVED METHOD FOR THE FORMATION OF REGULAR CRYSTALS.

By H. N. WARREN, Research Analyst.

FOR the formation of crystals, of a perfect and definite form, the method known as growing the same, aided by spontaneous evaporation, has, perhaps, ranked as one of the most successful. This, however, is, for the most part, considerably tedious, and, without a fair experience, often causes an experiment of long duration to terminate in the production of mal-formed specimens or of an exceedingly brittle structure. Thus, amongst the numerous crystallisable salts none are more distinguishable than the alums, both on account of their magnitude and their symmetrical appearance.

As an improved method of obtaining the same a concentrated solution of potash-alum was obtained by dissolving a pound of alum in about a litre of water, and placing the same in a bath maintained at a temperature of about 80° F. At the termination of an hour small but very perfect octahedrons were obtained, these were detached from their mother-liquor, selected, and placed aside for completion. The maternal solution was now cooled to 60° F., depositing a further quantity of agglomerated crystals, which were separated by decantation, and to the solution retaining the remainder of the alum were returned the selected crystals. The lower extremity of the vessel containing the same was next surrounded by a refrigerative mixture, composed of equal parts of potassic nitrate and ammonium chloride, in sufficient quantity to last for several hours, and placed in such a manner that the uppermost layer sustained a temperature of about 50° F., and containing a feeding tube, in which was inserted a further quantity of alum, and supplied at intervals, in order to replenish and sustain the strength of the solution. The small crystals, as obtained by the first operation, when subjected to this treatment, rapidly increase in size and shape; twin crystals, or small ones, which are apt to collect upon the sides, may be removed by the careful application of a smooth surface, of sufficient hardness, and washing with water. Chrome-alum thus treated yields most beautiful and perfect crystals. Not amongst the least beautiful may be mentioned those of potassium ferrocyanide, which appears of a transparency equal to that of glass.

Everton Research Laboratory,
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EXPERIMENTAL RESEARCHES IN THE REDUCTION OF THE DIFFICULTLY REDUCIBLE METALS.

By A. J. ROGERS.

(Concluded from p. 230).

THE melting-point of the double chloride is less than 200° C., while that of pure Al is 700° C., and of cryolite nearly 1000° C., so the Al is perfectly fluid and readily coheres when reduced from cryolite. At the same time, the temperature is not sufficiently high to volatilise the Al. Cryolite, or other fluoride, has the disadvantage, as compared with the double chloride, of tending to flux the containing vessel, and greater care is necessary in the selection of materials for crucibles or crucible linings, and the temperature must be kept as low as other circumstances will permit. There is little difference in the transfer resistance in either class of salts. The addition of chlorides of the alkalies, or of the alkaline earths, permits electrolysis with a somewhat lower electrical potential. It is probable that there is more solution of the metal, and diffusion and re-union of the ions generally, in the electrolysis of the double fluoride than of the double chloride. I have repeatedly passed a current of 60 to 80 ampères through pure melted cryolite for several hours without obtaining more than a grm. or so of the metal. In those experiments an alumina-lined clay crucible was used, containing 25 to 30 pounds of the salt, with carbon cathode at the bottom of the crucible and a similar carbon anode passing in at the top. A tight-fitting cover prevented access of air from the top. Drawing the electrode farther apart increased the yield of metal from the same number of ampères. Mechanical agitation, or boiling, of the liquid would also tend to convey some of the Al through the molten mass, and thus bring it in contact with the liberated fluorine. Cryolite, when solid, has a higher specific gravity than Al, but when liquid the Al will sink to the bottom of it. It is doubtless true that with the temperature very high, the liberated Na from the cryolite does not reduce the Al, but passes off as a vapour at the top of the bath, or re-unites with the fluorine, and thus only a small amount of Al would be deposited at the cathode. I think it hardly probable that the reduced Al converts the Al_2F_6 of the cryolite to a lower fluoride.

It is probable that Al_2F_6, when pure, is not an electrolyte, as the resistance increases as other salts present decreases. Prof. W. Hampe gives experimented proof in the *Chemiker Zeitung*, August 3, 1887, that the pure chlorides, bromides, and iodides are not electrolytes. That has been my experience with carefully prepared pure Al_2Cl_6. I attempted to pass the current from a 30 cell Grove battery in series, using carbon electrodes a sixteenth of an inch apart, in Al_2Cl_6 without any deflection of the needle of a sensitive galvanoscope. The melting of the Al_2Cl_6 was made to take place, and the circuit closed, under paraffin, and also in glass vessels in which there was no access of air. On account of the great volatility of the salt an exit was allowed for the large amount of vapour passing off in the melting. It is still more improbable that the oxide of Al is an electrolyte, although it is regarded as such by Heroult, in U.S. patent, August, 1888. He passes the current through Al_2O_3, using copper as negative electrode on the bottom of a carbon crucible, and a carbon rod as positive electrode, and extending down from the top nearly or quite touching the copper. A powerful current fuses the Al_2O_3, which, at this high temperature, in presence of the carbon and copper, is reduced, and forms with the copper aluminium bronze. That there is no electrolysis I am convinced from the following experiments:—

I passed a current of 80 ampères for half an hour through Al contained in a carbon crucible having copper in the bottom. Some time after fusion took place, the current was broken, and a sensitive galvanometer showed

no deflection of the needle when put in the alumina current.

There seemed to be no electrolytic conduction, inasmuch as the current did not pass with 50 volts if the carbon electrode did not form at least a loose contact with the copper, or was not connected by particles of carbon, Further, the direction of the current made no perceptible difference with the amount of Al set free to unite with the copper to form bronze. I also used an alumina crucible, with copper and platinum electrodes passing through the crucible nearly horizontally, and forming loose contact in the centre of the mass of alumina. No alloy of copper was formed containing Al, and no polarisation could be observed, though the fusion was complete, and, of course, with it the copper and platinum.

What I desire more particularly to present in the present paper are the results of some experimental work performed during the past three years, in the electrolysis of mixed NaCl and cryolite, using molten negative electrodes and more especially lead.

Lead (Pb), tin (Sn), zinc (Zn), cadmium (Cd), antimony (Sb), and bismuth (Bi) were used. They all readily alloy with Na, and these alloys will give up the greater part of the Na when placed in melted cryolite, and alloys of these metals with Al will be formed or the Al set free.

A large portion of the Na (or K) can be recovered from these various alloys by distillation in an iron crucible. They can be heated to a higher temperature than pure Na, or K, in acid crucibles without the Na, or K, attacking the crucible. One part of Na added to 9 parts of Pb and melted under paraffin forms an alloy (NaPb probably), which still retains much of the appearance of the Pb, though harder and more brittle, and when placed in water acts very slowly upon it.

One part of the Na to 4·5 parts of Pb (Na_2Pb) gives a brittle, almost granular, alloy, having a blue-black colour, and acts quite rapidly upon water.

One part of Na to 2·25 parts of Pb (Na_4Pb), forms a dark blue iridescent alloy, quite compact, with a smooth cleavage, and acts very rapidly when thrown upon water.

One part of Na to 1·5/6 Pb is less homogeneous than the preceding alloys, and cuts with a knife like Na.

One part of Na melted with 14 parts of Sn, under paraffin, gives an alloy that is not homogeneous, which is of a blue-black colour on the top of the mass, and of a hard, metallic, some what brittle character on the bottom, forming two distinct alloys.

One part of Na to 6 parts of Sn, melted under paraffin, gives a more homogeneous alloy than the first, and of a darkish compact character, not very brittle.

One part of Na to 3 parts of Sn gives a homogeneous mass of blue-black colour, melting at a point just above the boiling-point of paraffin and considerably above that of pure Sn.

One part of Na to 1 part of Sn gives a granular alloy that melts at about the melting-point of Sn. When thrown upon the water the Na unites with considerable energy with the water.

One part of Na to 0·5 part of Sn gives an alloy that cuts like Na, and resembles it in appearance, and when thrown upon water the Na unites with so much energy that the liberated H ignites, and the black powder of Sn falls to the bottom.

In a future paper I shall hope to give some of the physical and chemical properties of these alloys with varying amounts of Na and K.

In the following will be found a few typical experiments incidentally illustrating the preparation of a few of these alloys by electrolysis, and especially the preparation of Al and its alloys. In a large portion of this work a 40 volt 90 ampère dynamo machine was employed, and Ayrton and Perry's instruments for measuring volts and ampères were used.

The following experiment illustrates the formation of Pb and Sn alloys.

Experiment 1.—A current averaging 72 ampères and 33 volts was passed through melted NaCl contained in two No. P Morgan crucibles, arranged in series, or two hours. Each crucible contained 30 pounds of the salt. In the bottom of the first crucible was placed 104 grms. of Sn, and of the second 470 grms. of Pb, each serving as cathode, connection being made through the bottom of the crucible. A carbon anode passed through the cover of the crucible and extended to within three inches of the molten metal cathode.

The crucible containing the Sn cathode was nearest the fire, and consequently hotter, and had an average potential difference across the electrodes of 12 volts, while that containing the Pb cathode was 21 volts. At the end of two hours the carbons were removed, the liquid allowed to cool, and crucibles broken open. The Pb alloy formed was of an iridescent shining bluish cast, and quickly dimmed on exposure to the air. It had a smooth cleavage and was very brittle. About 400 grms. of the pure alloy were removed, and the remainder, with adhering NaCl, put in water, and the Na estimated by standard acid solution.

When a piece of the alloy was thrown into water the action was very energetic, and when the alloy was exposed to the air it rapidly oxidised, and absorbed moisture from the air, and became very warm. The bottom of the crucible was protected from excessive heat, and the alloy produced no perceptible action upon it. The total amount of Na as sodium hydroxide was 165 grms., corresponding to 96 grms. of the metal Na. The theoretical amount of Na deposited in two hours with 72 ampères is about 122 grms. The tin alloy formed a solid mass of one-half inch in thickness, and 4·5 inches in diameter. It had a fibrous or striated character in a vertical direction nearly or quite as soft as pure Na, and when freshly cut resembled Na somewhat in appearance, having a steel-grey or ash colour. It easily ignited spontaneously in the air, and when thrown upon water the energy was so great that combustion of the liberated hydrogen took place. In these rich alloys the Pb and Sn were found at the bottom of the vessel of water, in a finely divided state, after the Na had entirely united with the water. There were about 90 grms. of Na alloyed with the Sn. Some of this alloy was preserved under paraffin for more than a year with only slight oxidation of the Na upon its surface. These alloys reduced Al from cryolite, or the chloride of Al, though the Na does not entirely leave the Pb, and considerable Na vapour passes off from the melted cryolite.

Experiment 2.—This experiment was repeated under the same conditions, using 2 pounds cryolite mixed with 36 of NaCl in each crucible. About the same amount of Pb and Sn alloy of Na was obtained, together with a considerable number of small globules of comparatively pure Al. I collected the globules formed on the surface of the Pb alloy, and, after re-melting, first under NaCl then in the air, a single globule was obtained, weighing 3·256 grms., and having a specific gravity of 2·71. Traces of Pb were present. The amount was decreased by re-melting in the air. Three buttons of an alloy of Al and Sn in the crucible containing the Sn cathode together weighed 4·46 grms., having a specific gravity of 4·69. This would indicate that the alloy contained about 45 per cent of Sn, and 55 per cent of Al, which would approach the formula Al_6Sn. There seemed to be little metallic Al present in the SnNa alloy. The liquid was agitated several times during the electrolysis with a carbon rod. The PbNa alloy contained some Al, which could be precipitated as hydroxide of Al from the aqueous solution of the alloy by neutralising with acid.

Experiment 3.—In another experiment I passed a current, having an average of 54 ampères and 10 volts, for 5·5 hours, through a mixture of 1 part cryolite and 5 parts NaCl in a single crucible having 370 grms. Pb as cathode. Upon opening the crucible 25 grms. of Al in globules, quite free from Pb and Na, were upon the top of the PbNa alloy. This Al had a specific gravity of 2·67, and contained some iron and silicon from the cryolite and

crucible. The very brilliant PbNa alloy contained some Al which could not be extracted by heating in air, but could be obtained by heating under NaCl.

The amount of Na present was 120 grms.; not much less than the theoretical amount. This was produced by a current of 54 ampères and 10 volts, working 5·5 hours, which is equivalent to one electrical horse-power for four hours.

Experiment 4.—Another experiment with two crucibles having 500 grms. of Pb as cathode, and with a current of 80 ampères, for four hours, and salt 1 to 5 of cryolite and NaCl, gave in one crucible 4 grms. of Al in small globules, and in the other no Al, with but a trace in the PbNa alloy formed. It is thus seen that the Pb must acquire a certain richness of Na before the Na will part from it to reduce the Al from cryolite diluted with NaCl.

Experiment 5.— In another experiment with two crucibles I used 90 grms. Pb in one, and 12 grms. in the other, with 1 to 5 of the salts cryolite and NaCl. Current was acting for four hours, having 80 ampères and 20 volts in both crucibles. The crucible having 90 grms. of Pb had an average of only 6·5 volts, being hotter than the other, and contained 15 grms. of free Al, besides the PbNa alloy, while no free Al was found in the other crucible, which was continuously at a lower temperature during the electrolysis. Re-melting the PbNa alloy of the two crucibles with cryolite gave 75 grms. of Al containing some Pb, Si, and Fe, and had a specific gravity of 2·89.

Experiment 6.—In another experiment 75 ampères were passed through two crucibles in series, with 6 volts in one crucible and 15 in the other, acting 6·5 hours; 400 grms. Pb were used in each crucible. A few globules of Al were found in the 6 volt crucible, but none in the other. The most of the alloy was re-melted in cryolite, and gave 155 grms. of Al. Theory would give about 325 grms. The crucible having the greater voltage gave no more Al than the other, and the electrical energy could have been reduced one-half with the same result. The energy actually consumed was equivalent to one electrical horse-power working twelve hours, which, as above stated, might have been reduced to one-half that amount.

Experiment 7.—In another experiment, running through two crucibles for seven hours, with 75 ampères and about 5 volts in each crucible, I obtained from 500 grms. of Pb for cathode 105 grms. of a highly siliceous Al from one crucible and 75 from the other. The heat was very high in both crucibles, and the Na had eaten more than half way through the clay crucible.

Experiment 8.—Passed 80 ampères with 24 volts through four crucibles, in series, for six hours, using 1 of cryolite to 3 of NaCl, with 450 grms. Pb in each crucible. Crucibles were lined from the bottom half way up the side with alumina, and the heat was regular and not too high, and the crucible scarcely acted upon by the cryolite or Na or Al. When the dynamo was thrown out of circuit at the close of the work, there was a potential difference of 12·25 volts across the four crucibles in series for several minutes, making 3+ for each crucible.

Exner gives the potential of NaCl with carbon electrodes at about 2·2 volts. 250 grms. of quite pure Al were obtained, with a large amount of Na in the re-melting with cryolite. There was then actually obtained, besides all losses, in round numbers, 1 pound of Al to the electrical horse-power per day of twenty-four hours.

Experiment 9.—Passed current of 73 ampères, on an average for four hours, through four crucibles in series, with 5 volts in each of three crucibles, and 20 in the fourth crucible. Obtained about the same amount in each crucible, 50 grms., or about 200 in the four crucibles; 54 pounds of NaCl and 18 pounds of cryolite were used in the four crucibles. The crucibles were lined half way up from the bottom with alumina. The fourth crucible could have been worked by 5 volts by bringing the electrodes nearer together, or raising the temperature of the electrolyte.

The preceding are a few of a large number of experiments illustrating the preparation of Al and its alloys by electrolysis. From my work thus far I cannot give complete experimental data as to the practical yield of Al that can be obtained from a given quantity of cryolite, or other fluoride or chloride. Probably 8 to 10 per cent can be obtained from cryolite, where the theoretical yield is 12·85 per cent.

I have generally used carbon rods 2·25 inches in diameter as anodes. A sample of 0·708 grm. of this carbon, heated on platinum foil for four hours in the air, gave 0·003 grm. of reddish residue, insoluble in common acids. These rods, if kept from action of the air during electrolysis, would last for forty-eight hours without much erosion. Carbon plates and cylinders were used, but the solid rods proved better in practice.

It is stated in Watts's "Chemical Dictionary," under Fluorine, that Cl displaces the F in any fluoride. In the preceding experiments Cl was certainly given off in large amount. The gases from the crucibles were allowed, however, to pass up the chimney, and I have as yet had no opportunity of analysing them. I have used various basic linings for my clay crucibles, but alumina has thus far succeeded best. I tried some "shrunk" magnesia from basic steel works, but it contained so much iron that I could not use it. If free from Fe it might answer very well. Lime can not be used, as it fluxes very readily.

Analyses of various samples of Al, obtained by the use of a Pb cathode, showed Al varying in purity from 75 to 99 per cent. Silica was present in quantity varying from 25 per cent to a trace, and iron varying from 5 per cent to a trace, and admixed Pb varying from 3 per cent to 0. There was but little loss in the quantity of Pb, and it could be repeatedly used.

The very low voltage and large quantity of metal obtained for a given number of ampères would seem to promise much for this method of extracting Al. More than a pound of Al to the electrical horse-power for twenty-four hours has been actually obtained, and, undoubtedly, continued experience will give a much better result.

The best results, and in fact the only quantitative results that have yet been published, so far as I am aware, for the separation of Al by electrolysis, are reported by Dr. John Hopkinson of the Kleiner process, where 3 grms. were produced to the electrical horse-power per hour, which would be about one-sixth of a pound in twenty-four hours.

Dr. Hopkinson reports that they used 60 volts to keep the cryolite in a state of fusion and electrolyse the salt. I cannot at present refer to details of work on the obtaining of pure salts of Al as electrolytes, and of durable crucibles, free from Fe and Si, besides mechanical arrangements and devices.

THE PRECIPITATION OF MAGNESIA.

By L. BLUM.

Dr. Mohr recommends to precipitate magnesia, not with sodium phosphate (disodium hydrophosphate), but with sodium-ammonium phosphate. As evidence he communicates a number of experiments from which it would appear that the precipitation with the latter salt is more rapid and more complete. By precipitating more and more dilute solutions of magnesia mixture he arrived at a point where sodium phosphate no longer gave a precipitate, whilst sodium-ammonium phosphate still occasioned precipitation.

Mohr overlooked, however, a circumstance of great importance in analytical practice, *i.e.*, that the precipitates obtained with the latter phosphate settle with extreme difficulty, whilst in precipitation with sodium phosphate, if the prescribed conditions are observed, the

deposition and complete separation of the magnesian precipitate is effected in a few hours, so that Fresenius prescribes only twelve hours' settlement before filtration.

The author, in the analysis of iron ores and furnace-slags, has been much engaged with determinations of magnesia, in which the quantity found never exceeds four per cent. In these cases small quantities of magnesium-ammonium phosphate have to be thrown down in presence of considerable proportions of ammonium chloride and oxalate and free ammonia, as the precipitation is always effected after the removal of the lime.

If sodium-ammonium phosphate is used the liquid becomes at once very turbid. The precipitate is of an extremely fine crystalline texture, whereby the settling is uncommonly delayed. In general the supernatant liquid does not become perfectly clear, even in four days. If we filter without previous settling the liquid runs through turbid, even with a double filter. With larger quantities of magnesia, if, *e.g.*, 1 c.c. of magnesium-mixture is precipitated, this inconvenience (as Mohr previously observed) does not occur. The precipitation and the subsidence of the precipitate ensue almost instantaneously, and we may filter immediately without the liquid running through turbid.

If we use sodium phosphate for throwing down the magnesia the precipitation is not so rapid, and at the outset not so decided. The precipitate when once formed settles well in a few hours, and the filtration presents no difficulties. The precipitation is as complete as with sodium-ammonium phosphate, as is proved by the following experiment, which has been often repeated:—

Two portions of magnesia were thrown down, A with sodium phosphate and B with sodium-ammonium phosphate. The filtrates from magnesium-ammonium phosphate were mixed, A with sodium-ammonium phosphate and B with sodium phosphate. Both portions, after standing for some days, gave a trifling deposit, the origin of which is explained by a phenomenon observed by W. Hintz, that an excess of the precipitant diminishes the solubility of ammonium-magnesium phosphate in water containing ammonium chloride and ammonia.

For the precipitation of small proportions of magnesia as they commonly occur in ores and furnace products, sodium phosphate is, therefore, contrary to the view of Mohr, preferable to sodium-ammonium phosphate. For the qualitative detection of magnesia, on the other hand, sodium-ammonium phosphate is preferable, of course only in such cases where the detection of alkalies in the same liquid is excluded.—*Zeitschrift f. Anal. Chemie*, Vol. xxviii., Part 4, pp. 452—454.

University College, Gower Street.—A series of evening discourses on Selected Branches of Applied Chemistry, illustrated by experiments and diagrams, &c., will be delivered in the Chemical Theatre on Wednesday evenings, at 8, commencing on Wednesday, December 11. They will be opened with a short address by Sir Lowthian Bell, Bart., F.R.S., D.C.L., President of the Society of Chemical Industry, &c., &c., who will take the chair on the occasion of Dr. Wright's first discourse on Dec. 11. Course I.: Dr. C. R. Alder Wright, F.R.S. (December 11 and 18), on Scientific Investigation as applied to the Manufacture of Iron and Steel. Course II.: Dr. Ferdinand Hurter, Vice-President of the Society of Chemical Industry (January 15, 22, and 29), (1) On Fuel; (2 and 3) The Sulphuric Acid Chamber and Process, with Modern Theories of the Chamber Process. Course III.: Dr. Adolf Liebmann (February 5), on the Applications of Organic Chemistry in some of the more recent Developments of the Coal-tar Industry of Dyeing and of Therapeutics. Course IV.: Watson Smith, F.C.S., F.I.C., Lecturer in Applied Chemistry in University College (February 12 and 19), on the Applications of Chemistry to Domestic Economy and Sanitation.

RELATIONS BETWEEN THE COMPOSITION AND THE ABSORPTION-SPECTRUM OF ORGANIC COMPOUNDS.

By MAX. ALTHAUSSE and GERHARD KRÜSS.

By careful measurements of the absorption-spectra of a large number of organic compounds which have known relations to each other one of the writers has repeatedly investigated the connection between the spectrum and the composition of organic bodies.

The experiments were summarised about a year ago in a communication to the *Zeitschrift fur Physikalische Chemie* (ii., p. 312). It was found that almost without exception the introduction of methyl, ethyl, oxymethyl—*i.e.*, those groups which increase the proportion of carbon in a compound—and also of the carboxyl-group, there is produced a displacement of all the absorption-bands of a spectrum towards the red. On the other hand, a displacement of the bands towards the blue end of the spectrum ensues when an atom of hydrogen in an organic compound is substituted by a nitro- or amido-group.

The accuracy of these propositions has been repeatedly confirmed by an examination of substituted thionines, a selection of which has been placed at the disposal of the authors by Herr A. Bernthsen. They give an account of this research, as well as of some experiments which show that the introduction of hydrogen into an organic colouring-matter has a considerable, and, as it appears, a regular influence upon its spectrum.

The absorption-spectra of the following bodies were compared:—

1. *Thionine and Dimethylthionine Hydrochlorates.*—Each of these has, in its spectrum, three absorption-bands. The one situate nearest the refrangible end of the spectrum disappears on the dilution of the liquid just when the two other bands become separately visible and measurable. The maximum darkness of the several bands were measured in ten-millionths of the wave-length (Angström), as follows:—

	1st band.	2nd band.	3rd band.
Thionine hydrochlorate ..	606·5	587·4	5637
Dimethylthionine hydrochlorate	616·8	595·1	576·0

The wave-lengths of the thionine bands increased on the introduction of methyl, the absorptions being displaced toward the red.

2. *Symmetrical Dimethylthionine and Symmetrical Diethylthionine Hydrochlorates.*—These compounds display bands similar to the above, and the measurements of the wave-lengths were as follows:—

	1st band.	2nd band.	3rd band.
Dimethyl compound ..	616·8	595·1	576·0
Diethyl ,, ...	621·1	604·2	578·0

An addition of CH_2 here also displaces the absorption-bands towards the red.

3. *Tetramethylindiamine- and Tetraethylindiamine-sulphides.*—The alkylised indamine-sulphides have also spectra with three absorption-bands, but the least refrangible band lies so close to the red extremity of the visible spectrum that its wave-length could not be measured. The maximum darkness of the other bands were determined.

	1st band.	2nd band.
Tetramethylindiamine sulphide ..	651·8	596·3
Tetraethylindiamine ,, ..	656·5	604·2

4. *Thionoline and Methylen Violet.*—The alcoholic solutions of both these bodies, even when rather strongly diluted, transmit little but red light. After a considerable addition of alcohol the blue of the spectrum becomes clear, and two bands are visible, possessing the following wave-lengths:—

	1st band.	2nd band.
Thionoline	575·2	550·7
Methylen violet	597·4	558·4

5. *Dimethyldiethylthionine Chloride and Tetraethylthionin Chloride.*—The two main bands of the thionine spectrum become visible on the strong dilution of the solutions of these compounds, and their maximum intensities have the following wave-lengths:—

	1st band.	2nd band.
Dimethyldiethylthionine chloride ..	655·2	605·4
Tetraethylthionine „ ..	658·6	606·5

Here also an increase of the carbon of a compound displaces the absorptions towards the less refrangible end of the spectrum.

From the measurements of the thionine spectra it appears indifferent whether we study the spectrum of a base by observing its hydrochlorate, hydriodate, or any other salt. The bands peculiar to the base lie at the same part of the spectrum.

The Influence of the Introduction of Hydrogen upon the Absorption-spectrum of a Compound.

Hitherto nothing has been known as to the influence, if any, of the introduction of hydrogen into a compound upon the absorptions in its spectrum.

It seemed that this question might be partly solved by a careful spectroscopic measurement of the tetra-hydrated amine bases. Combinations such as diazobenzol chloride + α-naphthylamine and diazobenzol chloride + tetrahydro-α-naphthylamine were compared. The spectra of these and other bodies showed no even approximately measurable absorption-bands, but all these compounds have a sharp and rapidly measurable boundary of the absorption, which darkens the more refrangible end of their spectra. In order to recognise the influence of the introduction of hydrogen upon the position of the absorptions, this boundary was determined in the spectra of the solutions. The concentrations of these solutions were selected so that the number of grms. of the two substances to be compared were to each other as the molecular weights of these bodies. Thus, equal volumes of the solutions to be compared contained an equal number of mols., and on examining equal strata of these solutions the light had to pass an equal number of mols. of the compounds, hydrogenised or not hydrogenised. The position of the boundary of the absorption gives, thus, direct evidence on the influence of hydrogen upon the positions of the absorptions. From the measurements carried out it appears that an addition of hydrogen to an organic colouring-matter displaces the absorptions in its spectrum towards the blue.

Generally speaking the relations between the composition and the absorption-spectrum of a compound are identical with those between the colour and the composition of any substance; for the colour is the result of the light not absorbed by the compound. If a colouring-matter is examined by means of the spectroscope in such a manner that we measure accurately what kinds of light are transmitted by the technical solutions of the colouring-matter and what are lost by absorption, we can, in virtue of the laws above indicated, predict with tolerable accuracy what will be the colour of a substitution-derivative of the primary compound. If, *e.g.*, such compound has, in its spectrum, a band which absorbs the blue, then, by the introduction of methyl or ethyl, a body is obtained in the colour of which there comes into play more blue and less green. If the primary colour has an absorption-band in the red its colour will become redder by ethylation because the band will be displaced towards the ultra-red. The decision what will be the influence of the substitution of a colouring-matter by different groups will, according to the above results, be trustworthy only if the absorption-spectrum of the original colour has been previously studied. Such applications of the spectroscope will certainly, in many cases, prove of use in chromo-technics.—*Berichte der Deutsch. Chem. Gesellschaft*, Vol. xxii., p. 2065.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

(Concluded fom p. 227).

Aluminium brass is another valuable alloy made by combining aluminium bronze with zinc in different proportions. It is a close-grained, homogeneous, and tough metal. The torpedo shell before you is cast from this metal (the No. 2 grade).

Aluminium brass.	Tensile strength in castings.	Elongation.
No. 1 ..	23—27 tons per sq. inch.	10—14 p.c.
„ 2 ..	30—34 tons.	6—11 „

This allloy forges hot, and its special casting properties, its resistance to corrosion, its low specific gravity, render it valuable as a material for ship's propellers, stern, and rudder frames, pump-plungers and rods, valves, wheels, and pinions, and for hydraulic and engineering work generally.

A number of tests were made by order of the navy department of the United States of aluminium bronze and brass, as compared with United States gun bronze, with favourable results.

A blade could be made of it at least one-third thinner than cast-iron or any other bronze blade, and would be correspondingly lighter.

For cartridge shells these alloys cannot be equalled; their strength would enable a thinner and lighter shell to be used, with the advantage of not being corroded by the contained explosive. The use of aluminium bronze as a material for cannon was the subject of a paper read before the United States Naval Institute in 1887. As early as 1859 a mountain gun of this metal was cast and tested by the Committee of Artillery of France, with very favourable results, the high price of aluminium being then the only thing prohibitive of its widespread use for guns.

The following are some results of mechanical tests of aluminium bronze and brass:—

Compression Tests made at Watertown Arsenal, U.S.A.

Original length.	Shortened to ins.	Original diameter.	Increased to ins.	Ultimate strength.	Ultimate strength.	Specimens (casting).
Ins.		Ins.			lbs. per sq. inch.	
2·00	1·705	0·798	0·865	80,200	160,400	"A" 1 bronze.
2·00	1·525	0·798	0·914	76,800	153,600	"B" 2 bronze.

Transverse Strength.

Cross section of bar in sq. inches.	Length between supports. No. inches.	Breaking load in pounds.	Aluminium brass No. 2, cast in sand, tested at Milton.
1	12	8,100	

Deflection with 5000 lbs. load was but 0·04 inch, and permanent set 0·01 inch, showing remarkably high transverse elastic limit, great rigidity, and elastic resilience.

* Read before the British Association, Section B, Newcastle Meeting.

Tests of Aluminium Bronze and Brass.

United States Navy Department Tests.

	Mark or No.	Approximate composition. Cu.	Al.	Si.	Zn.	Sn.	Length between reference marks.	Diameter in ins.	Area in sq. ins.	Tensile strength.	Elastic limit.	Elongation per cent in 15 inches.	Reduction of area.	Diameter at fracture inches.	
							Inches.			lbs. per sq. inch.	lbs. per sq. inch.		Per cent.		
Aluminium bronze or brass.	1*c*	91·5	7·75	0·75			15	1·875	2·7612	60,700	18,000	23·200	30·7	1·56	Chill castings.
	7*c*	88·66	10·0	1·33			15	1·875	2·7612	66,000	27,000	3·800	7·8	1·80	
	9*c*	91·5	7·75	0·75			15	1·875	2·7612	67,600	24,000	13·00	21·62	1·66	
	10*c*	90·0	9·0	1·0			15	1·875	2·7612	72,830	33,000	2·40	5·78	1·82	
	11*c*	63·0	3·5	0·33	33·33		15	1·875	2·7612	82,200	60—73,000	2·33	9·88	1·78	
	11*d*	63·0	3·33	0·33	33·33		15	1·900	2·840	70,400	55,000	0·40	4·33	1·86	
	13*c*	92·0	7·5	0·5			15	1·875	2·7612	59,100	19,000	15·1	23·59	1·64	
	9*d*	91·5	7·75	0·75			15	1·900	2·840	53,000	19,000	6·2	15·50	1·75	Dry sand castings.
	10*d*	90·0	9·0	1·0			15	1·890	2·810	69,930	33,000	1·33	3·30	1·86	
	13*d*	92·0	7·5	0·5			15	1·930	2·930	46,550	17,000	7·80	19·19	1·73	
	1	88·0			2·0	10·0	15	1·875	2·7612	18,000	10,000	2·50	4·70	1·83	Green sand castings.
	2	88·0			2·0	10·0	15	1·875	2·7612	24,590	11,000	8·20	6·80	1·81	
	3	88·0			2·0	10·0	15	1·875	2·7612	22,500	11,000	5·80	10·89	1·77	
	4	88·0			2·0	10·0	15	1·880	2·7760	23,000	13,000	4·00	10·36	1·78	
	5	88·0			2·0	10·0	15	1·880	2·7760	20,570	13,000	2·33	6·30	1·82	
	6	88·0			2·0	10·0	15	1·880	2·7760	23,750	13,000	3·70	7·30	1·81	

Tests of Hardness of Large Bars.

Aluminium Bronze or Brass.

Mark.	Hardness of head.	Hardness of stem.
1*c*	9·39	13·85
7*c*	14·12	14·26
9*c*	11·18	13·59
11*c*	14·69	10·60
10*d*	17·08	16·07

Hardness of Navy Yard Bronze.

Mark.	Hardness of head.	Hardness of stem.
No. 1	3·33	3·33
„ 5	3·67	6·56

The Navy Yard bronze was furnished by the United States Government, and carefully cast at New York Navy Yard, under inspection of an officer detailed for that purpose.

William H. Harris,
Chief Engineer, U.S.N.

Tests made at Milton Works.

Description.	Original diameter.	Final diameter.	Original area.	Final area.	Original length.	Final length.	T S original section. Tons.	T S final section. Tons.	Elongation %.	Reduction of area.
Rolled No. 1 .. .. Brass	0·737	0·620	0·4266	0·3019	3·812	4·562	37·7	53·3	22	29·2%
Rolled No. 2 .. .. Brass	0·614	0·530	0·2960	0·2200	5·165	5·625	37·8	50·9	9·7	25·6%
Rolled "C" .. .. Bronze	0·731	0·400	0·4196	0·1256	6 ins.	8 ins.	34·3	114·6	33·3	70%
"Hercules" .. .. Metal rolled hot to 1¼ in.	0·607	0·485	0·2893	0·1847	2·56	3·47	34·0	53·6	35	36%
"A" bronze .. .. No. 2 brass	0·599	—	0·278	—	2·46	—	44·5	—	5·7%	10%
Rolled hot from 3 sq. in. pillar to 1¼ in., and cold to 1 in.	0·570	—	—	—	2·40	—	39·0 88,000 lbs.	—	12·5%	17·6%

Tests made to determine Effects of Temperature.

"A" aluminium bronze.	Diameter.	Length.	Tensile strength.	Elongation.
Cast in sand.. ..	0·330	1	116,000	5 not broken.
Duplicate	0·330	1	108,000	4 „ „
Same bar heated to 450° Fahr... ..	0·330	1	108,000	1 „ „
Cooled to temperature of room ..	0·330	1	109,000	„ „
Heated to 450° Fahr., or possibly somewhat higher temperature ..	0·330	1	86,000	5 bar broke.

Showing that this bronze retains its strength through a range of temperature. Aluminium brass No. 2 subject to like test broke at 29,000 and 35 per cent elongation, with very great contraction of area. When cold, the same bar resisted 85,000 pounds without rupture.

Aluminium Alloys.

Shrinkage per inch in 12 inches.

Aluminium Bronze.

	Dry sand.	Green sand.
A 1	1/11	1/8"
A 2	—	1/8"
A 3	3/32"	1/32"
C 2	—	1/8"

Aluminium Brass.

	Dry sand.	Green sand.
No. 1	$\frac{1}{8}$"	—
No. 2	$\frac{5}{32}$"	$\frac{5}{32}$"

Aluminium Hercules.

	Dry sand.	Green sand.
No. 3	$\frac{5}{64}$"	$\frac{5}{16}$"
No. 4	$\frac{5}{64}$"	—

Aluminium Bearing Metal.

	Dry sand.	Green sand.
No. 1	—	$\frac{5}{64}$"
No. 3	—	$\frac{1}{12}$"
Silicon	—	$\frac{1}{8}$"

Ferro-aluminium.—The alloys of aluminium and iron have long been known. They are referred to by Faraday, who found 0·013 per cent to 0·69 per cent aluminium in "wootz" steel. Rogers, in an article in the *Moniteur Industriel*, No. 2379, 1859, says a small per cent of aluminium makes steel hard, strong, and brittle; a larger quantity makes it very dense, without impairing its peculiar polish or detracting from its qualities.

The influence of aluminium in small quantity on cast iron is very marked, and was last year the subject of an interesting paper by Mr. W. J. Keep in conjunction with Prof. Mabery and L. D. Vorce, of the Case School of Applied Science, Cleveland, Ohio, U.S.A., read before the American Association for the Advancement of Science, August, 1888.

Two bases were used—one a white iron, with composition Si 0·186, P 0·263, S 0·0307, Mn 0·092; the other grey Swedish iron, marked F.L.M. with Si 1·249, P 0·084, Si 0·04, Mn 0·187. The ferro-aluminium used was made by the Cowles process, and contained Si 3·86, Al 11·42 per cent. Each based was experimented upon separately, and at the same time a series of blank trials were made, the metals in the two series being subjected to exactly the same conditions.

The following results were obtained:—

1st. *Solidity of Castings and Prevention of Blow Holes.*—The aluminium castings were of a slightly finer grain and of increased solidity, with 0·1 per cent Al present. The resistance to dead weight was increased about 44 per cent, and to impact 6 per cent.

2nd. *Does the Aluminium Remain in the Iron after Re-melting?*—The white base, after the addition of 0·25 per cent of aluminium, was re-melted six times, fresh quantities of the white base being added each time. That the aluminium remains in and improves the iron is shown by the superior and stronger castings obtained in this series, even after the percentage of aluminium had become very low, than in those cases where no aluminium was added.

3rd. *The Effect of Aluminium on the Grain.*—Aluminium seems to enable iron to hold in solution all its carbon until just upon the point of solidification, when it is precipitated in a finely graphitic form. The advantage of this is the uniformity of the mass and the absence of pockets of graphite, which are generally produced when ordinary grey iron has been cooled slowly. Hence the homogeneity and greated strength of the aluminium castings. The rapidity of cooling makes little or no difference, as the release of the carbon seems to be instantaneous, and only at the moment of crystallisation. A very little aluminium is sufficient to precipitate graphite from white iron, 0·25 per cent rendering it perceptibly darker in colour, 0·5 per cent more so, whilst 0·75 per cent renders it quite grey with no signs of white. With increasing amounts up to 4 per cent, the maximum in all these experiments, the effect is the same, the castings becoming softer and greyer as the amount of aluminium increases. The presence of much silicon does not alter the matter. The grain being the same also in thin, and rapidly cooled, as in thick castings.

4th. Aluminium castings are not affected by chilling; graphite is liberated whether the casting is cooled rapidly or slowly, with the result that the grain is uniform, and there is no chill.

5th. When sufficient aluminium is present to liberate the graphite, a coating is formed on the casting which resists the sand and the heat, and prevents the iron burning the sand into itself.

6th. The fineness of the grain causes them to be more easily cut than cast-iron of coarser grain.

7th. The presence of aluminium increases the strength to sustain a constant load, but the strength does not increase uniformly with the percentage of aluminium.

8th. The increase in strength is much greater and more marked than in the preceding. Above a certain percentage the strength diminishes, due to larger amount of graphite liberated.

9th. Elasticity is improved.

10th. The fineness and compactness of iron containing aluminium gives less permanent set than iron equally as soft when that softness is produced by silicon.

11th. The shrinkage is slightly increased with a small quantity of aluminium, due probably to the elimination of blow holes; but with 0·75 per cent, and more, it is much decreased, especially in case of wrought-iron.

12. In case of the white iron fluidity is much increased —with grey base containing much silicon it is not so clear, though it is believed the fluidity is increased.

The fact that aluminium lowers the melting-point of iron is utilised in the Mitis castings, the invention of Mr. Peter Ostberg, of Stockholm. In making Mitis castings a very small quantity of aluminium, about 0·050 per cent Al in form of 7 or 8 per cent ferro-aluminium, is added to the charge (about 60 lbs.) of wrought-iron in the crucible the moment this has been melted. The fusing-point is at once lowered about 500°, and the charge becomes very fluid and can be cast in the finest moulds. The great difference between its temperature and its fusing-point gives all the time necessary for its manipulation without danger of its solidifying.

The tensile strength of Mitis castings may be as high as 27 tons per sq. inch, with an elongation of 20 per cent.

Another alloy made in the electric furnace is silicon bronze, which, owing to its great strength and tenacity, its resistance to corrosion, combined with high electrical conductivity, is perhaps the best metal extant for electric light, telephone, and telegraph wires.

In conclusion, may I direct your attention to the test bars, castings, and specimens of aluminium alloys made by the Cowles process, kindly lent for this paper by the Cowles Syndicate Co., Limited.

Specimens of Aluminium Alloys Made by Cowles Process.

Exhibited in connection with Paper read before B Section, British Association.

No. 1. Aluminium bronze cylinder (Torpedo shell), 2 feet long, 14 inches diameter, cast in sand with core; outside finely polished, inside rough.

Test bars taken from same pouring gave—

Tensile strength, 105,000 lbs. per sq. inch (46·87 tons).

Elongation, 6 per cent.

No. 2 Cylinder, same as above, made from aluminium brass "No. 2" (one-third zinc) (33·3 per cent).

Tensile strength, 90,000 lbs. per sq. inch (40·17 tons).

Elastic limit, 66,000 lbs. per sq. inch (29·46 tons).

Elongation, 6 per cent.

No. 3. Piece of calico-printing cylinder, 6 inches diameter and about 1 foot long, cast by Messrs. Bolton and Sons, Oakamoor Mills, Cheadle, Staffordshire, in the same manner as they cast their copper cylinders.

No. 4. Dynamo hub of aluminium brass, No. 2.
This metal has a tensile strength of 93,000 lbs. to the sq. inch, and 5 per cent elongation.
The German silver that has heretofore been used in the Brush hubs has but 44,000 lbs. tensile strength and 24 per cent elongation, and costs much more than this brass.

No. 5. Billet of 10 per cent aluminium bronze, cast in chill; one entire side polished to show perfect casting, colour, &c.

No. 6. Lathe turnings of aluminium bronze, showing no signs of oxidation after three years' exposure to the atmosphere.

No. 7. Aluminium "pig" casting (80 per cent aluminium), produced directly by heat of electric furnace. Reduction of oxide of aluminium by carbon (believed to be the first reduction by carbon of this oxide).

No. 8. North Metropolitan (London) Tramway Co.'s "car-bearing" of ordinary gun metal after a year's wear, and originally of same dimensions as No. 9.

No. 9. Same Co.'s car-bearing made from Cowles' aluminium bearing metal after a year's running on same route as No. 8, no wear being perceptible.

No. 10. Aluminium bronze bar, one end hammered hot, other end twisted cold.

No. 11. 5 per cent aluminium bronze bar, bending test, bent cold.

No. 12. 11 per cent aluminium bronze rolled sheet, test spring by bending.

No. 13. 5 per cent aluminium bronze rolled bar, tested at Phœnix Works, Ruhrort, Germany.
Tensile strength, 82,880 lbs. to the square inch (37 tons).
Elongation, 60 per cent.

No. 14. 5 per cent aluminium bronze cup, drawn cold from a 9 inch disc.

No. 15. Sample of silicon copper product run direct from furnace; silicon = 15·08 per cent.

No. 16. Bar of basic Siemens steel, tested at Phœnix Works, Ruhrort, Germany, showing bending and fracture.

No. 17. Bar of 10 per cent Cowles aluminium bronze, tested at Phœnix Works, Ruhrort, Germany, showing bending and fracture.

No. 18. One inch round bar of aluminium bronze.

No. 19. Two inch square bar of aluminium.

No. 20. Propeller blade of No. 2 aluminium brass.

No. 21. Ores, slags, fragments of carbon from the electric furnace.

No. 22. Drawings and views of the electric furnace, engine, dynamo.

No. 23. Photographs of the Cowles Aluminium Works, Milton, Staffordshire.

NOTICES OF BOOKS.

Coloured Analytical Tables showing the Behaviour of the More Common Metals and Acids with the Ordinary Reagents, with Special Reference to the Colour of the Various Oxides, Salts, Precipitates, Flames, Borax-beads, and Blowpipe Reactions. A Class-Book for Students in Hospitals, Colleges, and Schools. By H. Wilson Hake, Ph.D., F.I.C., F.C.S. London: G. Philip and Son.

The novelty of this work lies in the coloured illustrations. In the general table we find figured a portion of a small test-tube as containing a portion of a precipitate coloured as nearly as possible to the reality. This direct appeal to the eye will very probably help the student who has seen the experimental production of the precipitate to remember its appearance better than would a mere verbal description. The same system is followed as far as possible throughout the work.

As part and parcel of the necessary reaction against verbalism this little book has its merits.

Manures and their Uses. A Handbook for Farmers and Students. By A. B. Griffiths, Ph.D., F.R.S.E., F.C.S. London: G. Bell and Sons.

This work belongs to the valuable "Agricultural Series" now in course of issue by the publishers. It reminds us in many respects of the author's "Treatise on Manures," but it contains several improvements, and it is addressed more especially to the former. The author commences with an account of the rise and development of British agriculture, showing its alternating stages of prosperity and depression. It seems to us, in these days, strange to read of wheat being, in the Roman epoch, systematically exported from Britain to Germany and Gaul. At the same time our island supplied the Roman Empire with horses, cattle, cheese, and with chalk, lime, and marl for use as manures. In the thirteenth and fourteenth centuries it appears that the outside yield of wheat per acre was only 10 bushels.

The first crude outline of an agricultural chemistry seems to be due to Sir H. Platt in 1594. Bone-dust was first used by Colonel St. Leger on his farm near Doncaster in 1765, but it was not generally adopted for seventy years later.

The author cannot accept the doctrine of M. Ville that no soil needs any other addition save nitrogen, potash, lime and phosphoric acid, and insists upon the necessity of supplying what may be called the minor elements of plant-food in an available form. He agrees, however, substantially with M. Ville in holding that chemical analysis alone is no adequate clue to the requirements of a soil. Potash and phosphoric acid may be present in fair quantity, but if they are in a condition insoluble in water and in the acid secretions of the roots of plants the land will prove barren. The eight laws laid down on p. 20 as regulating the productiveness of a soil strike us as being eminently judicious. The last of them, we fear, too often escapes the attention of agriculturists. It is this:—"The manure produced in the course of husbandry is *not* sufficient to permanently maintain the fertility of a farm; it lacks the constituents that are annually exported in the shape of grain, hay, milk, and live-stock."

The table given on p. 24 arranges manure under the three heads of organic, artificial, and special. We can scarcely accept this classification, since there figure under the second head lime, gypsum, salt, silica, &c., which cannot be called "artificial." The table given on the opposite page, where manures are grouped according to the constituent which they supply to the soil, is preferable. Dr. Griffiths endorses the conclusion of M. Ville, that "the farmer who uses nothing but farmyard manure exhausts his land."

The action of certain microbia in inducing putrefactions and nitrification in manure heaps is here brought into the necessary prominence.

A temperature of 150° F. is fixed as the maximum permissible, and the use of a solution of ferrous sulphate is recommended for preventing the escape of ammonium carbonate. He has ascertained experimentally that peat-litter yields a better manure than straw-litter. A very serious defect of farmyard manure which, we think, has escaped the notice of M. Ville, is that it is "a medium in which fungoid diseases, such as the potato-disease, wheat-mildew, &c., are capable of hibernating for months without losing their vitality." Dr. Griffiths adds that "the wise farmer will never use farmyard manure obtained from turnip-fed cattle for turnip-crops."

Irrigation, the author thinks, should be practised only upon porous and well-drained soil. He speaks of the sewage farms in the neighbourhood of Paris as sending

their produce of vegetables to the Halles Centralles. The yield is certainly abundant, but the crops generally come later than those from non-irrigated soils, and hence command a lower price.

In the section on bone-manures the author quotes Liebig's terrible denunciation of England for denuding the world of bones and other mineral matter, and then letting the resulting excreta flow down into the sea. Of course, where we utilise sewage either by irrigation or by a precipitation process which yields manure, we no longer incur this censure. But where we still let it run down to the sea continuously or intermittently, or, worse still, where we precipitate the sewage and carry the deposit out to sea, we are guilty.

Want of space does not permit us to carry any further our examination of this valuable work, but we can conscientiously recommend it to the careful perusal of all persons interested in agriculture.

Notes on Qualitative Analysis; arranged for the Use of Students of the Rensselaer Polytechnic Institute. By W. P. Mason. Troy, New York: Nims and Knight.

The peculiarity in virtue of which Prof. Mason asserts that his work has a definite *raison d'être* is the frequent reference made to standard authorities, such as Fresenius, Watts's "Dictionary," Roscoe and Schorlemmer's great work, &c. It will doubtless be very useful for the student thus to fill in the necessarily meagre outline given in the text. But what of the many students who have not access to a well-stocked library? Would they not prefer a treatise which should at once supply all the information they require?

A commendable feature is that the student is recommended to use the spectroscope, *e.g.*, for the recognition of traces of potassium, and for distinguishing calcium from strontium.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—Herr Wollheim, in his letter (Chemical News, vol. lx., p. 221), claims that the Amines sludge is so "permanently" sterilised that it will uot decompose even when placed upon the land. It is interesting to note with what this amount of work is done, and what are the results, so far as the manurial value of the sludge is concerned when it is done.

Herr Wollheim's last declaration is that he uses 6½ ounces per 1000 gallons, or 2·843 grains of herring-brine per gallon. Allowing it to be correct that herring-brine contains two-thirds of a percentage of trimethylamine, or a salt of that body equivalent to that quantity, then we should get 0·01876 of a grain per gallon. This, then, is the quantity, or its equivalent as "Aminol," which does the work. Allowing that this quantity can disinfect sewage, and even carry its powers with the sludge, so that the latter will not decompose when applied to land, then, as it appears to me, he has over-reached his prime object in putting it there; for he renders his sludge useless as a manure. The nitrogen of good sewage sludge is nearly all present as organic nitrogen, and therefore is not plant food until after decomposition or nitrification. "Permanent sludges" and undecomposable sludges, therefore, must remain on the land for ever as such, or, at all events, until the wonderful powers of "Aminol" have been exhausted.

It is passing strange that in order to liberate 0·01876 of a grain of trimethylamine such a large quantity of lime is needed.

In my opinion from 45 to 50 grains of lime per gallon are quite impracticable quantities when applied to large flows of sewage. Awaiting "certain investigations,"—I am, &c.,

Cyclops.

DETECTION OF ADULTERATION IN ESSENTIAL OILS.

To the Editor of the Chemical News.

Sir,—I was much interested in reading the article by Mr. Rowland Williams, on iodine absorption of essential oils, which appeared in the Chemical News, vol. lx., p. 175.

In connection with the examination of oil of peppermint for adulteration with oil of turpentine, I had occasion to employ the iodine absorption of the oils, and found it extremely useful. The work was somewhat extended, and determinations of the iodine absorption of a number of oils were made. The results were published in *The New Idea*, Detroit, Mich., U.S.A. (March, 1889, p. 17). The article on oil of peppermint was given in the same issue. These articles were repeated in the *Pharm. Journal and Trans.* (London) for July 6, 1889, p. 4, and June 29, 1889, p. 1056. The article on oil of peppermint was reprinted in the *Journal of Analytical Chemistry* (Easton, Pa., U.S.A.), for July. Closely following my results, Mr. R. H. Davies independently published in the *Pharm. Journal and Trans.* (London), April 13, 1889, p. 821, an exhaustive paper on this same subject of iodine absorption of essential oils. In searching after literature on the subject, Mr. Davies found that Mr. C. Barenthein, a pharmacist of Berlin, had given in the *Archiv de Pharm.*, October, 1886, determinations of the absorptions for eleven essential oils. So far as I know at present, the work of Mr. Barenthein is the first in this line.

The last six months have given us quite a literature on this subject, and all goes to show that "original work" is properly only the expression of prevailing tendencies. I have gone at some length into these references in the hope that they will be of interest to Mr. Williams and others, as they would be to me under the same conditions.—I am, &c.,

H. W. Snow.

Detroit, Mich., U.S.A.,
October 25, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 233) Mr. W. Johnstone contends that *all* the fat can be extracted from a milk by a modified Wanklyn process. The higher results obtained by the paper-coil process, he says, are due to the increase of weight produced by oxidation. How then does he explain that similar higher fats are given by the (1) Soxhlet areometric process; (2) the lactocrite; and (3) by the Schmid process, where there can (in the first, certainly), be no pretence of oxidation. It is singular that all these should agree with the calculated results, and with one another, in giving higher fat than the now generally discarded Wanklyn method.—I am, &c.,

Alf. W. Stokes, F.C.S., F.I.C.

Analytical Laboratory,
Vestry Hall, Paddington Green, W.
Nov. 11, 1889.

New Process for Preparing Oxamide and Oxamic Acid.—E. Matthieu-Plessy.—The author introduces ammonium oxalate into ammonium nitrate in fusion, and keeps the mass at 170° to 175° for four hours. On treating the mass with water he obtains oxamide and oxamic acid.—*Comptes Rendus*, Vol. cix., No. 17, Oct. 21, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 17, October 21, 1889.

Researches on the Relations which Exist between the Physical Characters of Plants and the Richness of the Soil in Fertilising Elements.—Georges Ville.—The characters of the plants which the author takes into consideration are the colour, the stature, and the entire weight. To limit the question he confines his studies to a single plant, hemp. These points are shown in an illustration which gives the comparative height of the plants, the weight of the crop, and the colours as seen in masses. The experiments were made with seven soils:—"Intense" manure (100 kilos. nitrogen), "complete" manure (75 kilos. nitrogen), manure without nitrogen, manure without phosphates, manure without potash, manure without lime, and soil without any manure. It must be remarked that M. Ville considers that plants require a supply of lime over and above that naturally existing in the soil, that present in combination with phosphoric acid, and that existing in the state of sulphate formed in the manufacture of superphosphate, and that he adds such further amount of lime in the form of gypsum. The hemp plants treated with "intense manure" were of the deepest green, reached the height of 1·53 metres, displayed the deepest green colour, and weighed 11·22 kilos. The plants with "complete manure" grew to 1·20 metres, were of a less deep colour, and weighed 11·15 kilos. Those without nitrogen reached only 0·61 metres were of a yellowish green, and weighed 4·74 kilos. Those without phosphates were 0·97 metre in height, were of a medium green, and weighed 8·22 kilos. Those without potash were only 0·40 metre in height, of a yellowish green, and weighed 5·22 kilos. Those without lime grew to 1·15 metres, were slightly paler than those without phosphate, and weighed 10·57 kilos. Lastly, the plants in unmanured soil were only 0·18 metre in height, were of a pale green colour, and weighed only 2·175 kilos. The author proposes to give in a future paper the determination of the proportions of chlorophyll and of carotine in plants differently manured.

The Simultaneous Synthesis of Water and Hydrochloric Acid.—P. Hautefeuille and J. Margottet.—In presence of chlorine or carbon monoxide the separation of the elements of water under the influence of heat determines the formation of gaseous mixtures, concerning the composition of which we have few accurate data. The authors have taken up the study of the decomposition of water under these conditions, and, before explaining the results reached when operating directly upon the vapour of water, they make known the composition of the mixtures formed in the synthesis of water in the presence of chloride, or in the synthesis of hydrochloric acid in the presence of oxygen. If the volume of chlorine in a gaseous mixture is greater than half the volume of the hydrogen in a gaseous mixture the number of equivalents of water and hydrochloric acid is always less than unity, and it decreases rapidly as the proportion of chlorine in the mixture increases. When the volume of the chlorine is double that of the hydrogen the water formed on the passage of the electric spark ceases to be appreciable. The weight of the chlorine remaining free is exactly half the weight of this gas introduced into the eudiometer. Every change in the proportion of chlorine added to the detonating mixture modifies the result. It is impossible to extend the mixtures containing chlorine; the law announced by Bunsen in consequence of his experiments on the combustion of mixtures of carbon monoxide, hydrogen, and oxygen, for the relation between the water and the hydrochloric acid formed in the combustion does not vary abruptly, but continuously on the progressive addition of chlorine to the detonating mixture. As regards the synthesis of hydrochloric acid in presence of oxygen, the authors find that the relation of the numbers of equivalents of water and hydrochloric acid formed by the combustion of mixtures obtained on adding oxygen to the elements of hydrochloric acid, is always less than unity, but it varies only within narrow limits on increasing the relation of the volumes of hydrogen from $\frac{1}{4}$ to 3.

On the Existence of Phosphonium Sulphate.—A. Besson.—If dry gaseous hydrogen phosphide is passed through pure sulphuric acid refrigerated down to −20° or 25° it is absorbed in quantity, and the liquid becomes syrupy. The product of the reaction is stable, and may be preserved if kept at some degrees below 0°. If the syrupy liquid is decanted out of the tube in which the reaction has taken place a solid white mass is found at the bottom, which seems to be crystalline phosphonium sulphate.

The Action of Ammoniacal Copper Sulphate upon Sorbite and Mannite.—M. Guignet.—A reply to the observations of MM. Vincent and Delachanal. The author has never denied that sorbite precipitates ammoniacal copper sulphate. On the contrary, he has affirmed "that mannite, dulcite, and probably the other isomers, produce at once blue precipitates in the solution of ammonium-copper sulphate."

The Part played by Ammonia in the Nutrition of the Higher Plants.—A. Müntz.—The author's experiments distinctly prove that the higher plants can directly absorb ammoniacal nitrogen by their roots, and that consequently the nitrification of ammoniacal manures is not a necessary condition for their utilisation.

Photometry with Nitrogen Iodide.—G. Lion.

MEETINGS FOR THE WEEK.

WEDNESDAY, Nov. 20.—Society of Arts, 8. First Ordinary Meeting. Opening Address of the 136th Session by the Duke of Abercorn, C.B., Chairman of the Council, and Presentation of Prizes.

AMERICAN MINERALS.

AFTER the close of the Universal Exposition

Prof. A. E. FOOTE

will remain at his Branch,

14, RUE DESAIX, PARIS,

until the 15th of December. Here he will be glad to meet collectors and to fill all orders received previous to that time. He finds it necessary to prolong his stay in Paris for the purpose of giving attention to the numerous orders for Minerals which have been received by mail, and which he could not fill on account of being constantly occupied with customers at his branch.

Many of the rare and choice Minerals shown at his Exhibit during the Exposition will be removed to his store. Here also will be found the most beautiful Red Vanadinites ever seen, with Crystals remarkable for large size and brilliant colour, and at very low prices; really showy specimens are sold at from 2s. to 5s. Also beautiful Red Wulfenites from Arizona; fine single crystals are sold at from 1s. to 5s. Among the other remarkable Minerals are Gadolinite, Colemanite, Hanksite, Thenardite, Apophyllite, Sperrylite, Beryllionite (new Glucium Species described by Dana), &c.

Specimens sent on approval. Especial attention is called to these beautiful minerals for Christmas and other presents.

PROF. FOOTE has, at his principal store, 1223, BELMONT AVENUE, PHILADELPHIA, U.S.A., the largest stock of Minerals, Chemical, and other Scientific Books for sale in the world, and will exchange for good minerals or for books. Send for Catalogue, specifying in what branch you are interested.

THE CHEMICAL NEWS.

Vol. LX. No. 1565.

AN EXPERIMENT IN COLOUR-BLINDNESS.*

By JOHN SPILLER, F.I.C., F.C.S.

Examination of several colour-blind persons having convinced me of the practical value of a compound tassel of green and grey silk cords as a preliminary indicator of defective colour-vision; and, moreover, having studied Professor William Pole's interesting memoir—describing his own case—in the *Philosophical Transactions of the Royal Society*, April, 1859, which is illustrated by a diagram, showing bands of "neutral grey" appearing to him in the middle of the green and at the deepest red, or crimson, of Chevreul's coloured *cercle chromatique*; I felt very desirous of trying an experiment to see for myself whether it was possible by the administration of a small dose of santonine—which is said to cause temporary colour-blindness—to realise in my own case the imperfection of vision which seems common to most colour-blind patients.

Such an experiment I made on the 29th of August; but before proceeding to describe the result it should be mentioned that I have good proof of my being blessed with the possession of a normal sight; for in the course of a long experience with coal-tar colours, and having frequent occasion to compare observations with regard to slight differences of tint with my six colleagues, I have never perceptibly deviated from the consensus of the laboratory staff, and may fairly claim to be reliable on this score. On a fine day, provided with an ample selection of chemical specimens and coloured objects, and Ladd's direct vision spectroscope ready to hand, I took, fasting, a small dose of santonine, a grain and a half, dissolved in a small quantity of alcohol and diluted with water. In less than five minutes the drug had taken effect; the white table-cloth appeared of a delicate bluish green colour—pale turquoise, exactly like the colours of the *Nineteenth Century Magazine*, and all objects were seen as through spectacles of that precise tint. A rapid survey was made of my varied collection of objects, and I went into the garden to use my spectroscope. I could see all the solar colours in unbroken series with scarcely perceptible variation; the Fraunhöfer lines were there as usual (not thickened), the violet extending up to the usual limit, and so with the red end, with slightly diminished brilliancy, but hardly appreciable absorption; there was *no neutral grey band in the green*, but this portion of the spectrum appeared quite normal and splendidly brilliant. The observation was repeated a few minutes later with the same results.

Turning to my coloured specimens. Nickel, copper, and iron sulphates, iodide and chromate of lead, ultramarine, and ammonio-sulphate of copper, were quite normal; oxalate of cobalt had not lost its delicate pink colour, nor nitrate of uranium its well-known shade. On the other hand, scarlet iodide of mercury was decidedly dulled, and a fine sample of carmine appeared more like crimson. By running my eyes along the book-shelves in my library, I soon noticed that "Gmelin's Chemistry"—Cavendish Society series—and other old-fashioned green bindings assumed a kind of slatey appearance, crimson backs appeared as maroon, dark brown was converted to chocolate, but I could see violet quite well, bright green pretty much as usual, the Chemical News, bound in scarlet, appeared red, and neutral grey bindings looked only darker in colour. I could see quite distinctly the difference between light-green and slate-grey silk tassels, so that my condition was not so abnormal as many of my colour-blind friends, who fail to see any radical tint-distinction between these two dissimilar colours.

Now for a word of caution. I had taken only what might be described as a quarter-dose—"2 to 6 grains" is the stated quantity in "Martindale's Extra Pharmacopœia"; other authorities say more—but at the end of fifteen or twenty minutes, the tension upon my nervous system proved so serious that I feared the worst consequences. I felt so giddy and depressed, with a kind of mild tetanus, that I was obliged to resort to an emetic—mustard and warm water,—which soon gave me relief. I would earnestly warn my readers of the danger of repeating this experiment; and now, on fuller enquiry, I learn that santonine is a drug reported to be "sometimes uncertain in its action," and occasionally developing "poisonous symptoms from its depressing effects on the nervous system." I had read of Dr. W. G. Smith taking a 5-grain dose to induce colour blindness—"Cooley's Cyclopædia of Practical Receipts," p. 1460—without dangerous consequences, and resolved to take a very much smaller quantity, 1½ grain, in the first instance, well knowing that more than this had often been given to children. Perhaps taking it in the state of solution, and before breakfast, or a wrong dose, made all the difference. However that may be, I shall never again try ophthalmic experiments with santonine, and would warn others against doing so without proper medical advice.

My object is accomplished: I wanted to search for Professor Pole's neutral grey bands in the solar spectrum, as he sees them in Chevreul's famous *cercle chromatique* diagram, but did not find them. Nor, it may be added, do any of my colour-blind friends see any break in the solar spectrum, although we know that the heavy green pigments are by them so often mistaken for grey. Furthermore, it does not appear that santonine gives the *same kind* of colour-blindness as commonly presented by the natural defect, or my colour test of green and grey would at once have indicated it.

London, September 2, 1889.

* Read before the British Association, Section A Newcastle Meeting.

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

The Committee, which was appointed at the Bath meeting with the object above mentioned, requested the co-operation of several gentlemen of special experience in the analysis of iron and steel, and is at present constituted as follows:—Professor Roberts-Austen (Chairman), Sir F. Abel, Professor Langley, Mr. Edward Riley, Mr. G. J. Snelus, Mr. John Spiller, Professor Tilden, and Mr. Thomas Turner (Secretary).

The Committee has held several meetings during the year, and considerable correspondence has taken place in connection with the matters which it was appointed to consider. Ultimately, the objects of the committee were defined, and a number of suggestions were drawn up in order to assist in carrying out these objects. These suggestions were then published in various technical papers, before being finally revised, in order to allow persons interested to make any further suggestions which might appear advisable. After revision these proposals assumed the following form:—

Objects.

It is proposed that the Committee shall co-operate with other similar Committees in the more important iron-producing countries, in order to provide standard

* Report of the Committee, consisting of Professor Roberts-Austen (Chairman), Mr. T. Turner (Secretary), and Professor J. W. Langley, appointed to consider the best method of establishing International Standards for the Analysis of Iron and Steel. Drawn up by Mr. Thomas Turner (Secretary). Read before the British Association, Section B, Newcastle Meeting.

specimens of iron and steel, the chemical composition of which shall have been carefully determined. The specimens adopted as standards shall be entrusted to some recognised official authority, such as the Standards Department of the Board of Trade, and shall be used either for reference in the determination of the accuracy of any proposed method of analysis, or for controlling the results of analyses in any cases of importance which may from time to time arise.

Suggestions.

1. Professor J. W. Langley, of the University of Michigan, U.S.A., to be requested to superintend the production of the samples; these to be prepared and preserved in accordance with the directions to be furnished by the Committee, and an equal portion of each sample to be forwarded to the several Secretaries of the respective Committees in the United Kingdom, America, France, Germany, and Sweden.

2. The Specimens, which are eventually to be adopted as standards, to be supplied to not more than seven representative chemists of repute in each of the countries above mentioned, who shall be requested to analyse the specimens by any method or methods they may prefer.

3. In the event of the analyses giving results which, in the opinion of the Committee, may be regarded as sufficiently concordant, the means of the analytical results of each of the several constituents to be adopted as representing the composition of the standards. The report on the analytical results not to be issued before the various analysts to whom the samples have been submitted shall have had an opportunity of examining it. The standards to be hereafter distinguished only by letters or numbers.

4. The attention of the Committee to be for the present confined to five samples of steel, selected as containing as nearly as possible 1·3, 0·8, 0·4, 0·15, and 0·07 per cent of total carbon, respectively. In addition to the determination of the amount of carbon present in each condition, the phosphorus, sulphur, silicon, manganese, and chromium also to be determined.

5. 200 kilos. of the samples selected for examination as standards to be prepared in all. This would give, after allowing sufficient for the required analyses, quite 5 kilos. of each standard for each of the five countries interested. Allowing, say, 10 grms for each applicant who might desire to use the standards, this would permit of 500 appeals to each of the five standards in each country, or at least 12,500 appeals in all.

6. The metal of which the samples are to be produced to be cast in small ingots, special care being taken to prevent any irregularity of composition. After the removal of the outer skin the metal to be cut by a blunt tool in the form of thin shavings, and mixed as intimately as possible.

7. The samples thus prepared to be preserved in separate small quantities (say of 30 grms. each), which shall be hermetically sealed in glass tubes so as to prevent oxidation.

8. The samples to be analysed, in the United Kingdom, by Mr. A. H. Allen, Sheffield; Mr. W. Jenkins, Dowlais; Mr. G. S. Packer, Steel Company of Scotland; Mr. J. Pattinson, Newcastle-on-Tyne; Mr. E. Riley, London; the Royal School of Mines; and Mr. J. E. Stead, Middlesbrough.

Progress of the Work.

Under date July 14, 1889, Professor Langley states that he has not as yet received a conclusive reply from the State Department at Washington to his application asking the Government to forward the samples through its consular agencies, so that they might reach their destination with the seals of the American Committee unbroken by the Custom House inspectors. The first four standards are ready to go as soon as word is received from Washington. They are packed in lead-lined hermetically sealed boxes, four for each country, and which are enclosed by a larger wooden case, the whole weighing about 400 lbs.

The material was prepared as nearly as possible in accordance with the directions of the British Association Committee. Ingots of crucible steel were selected from a lot of some twenty-five tons, which came nearest to the required carbon for the first three standards. The last, C=0·15, was too low to be made in a crucible, for, after melting up a number of charges, it was not found possible to get below 0·20 in the plumbago crucibles used. Professor Langley accordingly took a large billet of Open Hearth Steel, and, after forging, had a piece weighing about 100 lbs. cut out of the centre.

The original weight of the ingots was 90 lbs., but, after turning off the skin and allowing for the pipe and some inevitable loss in turning, not much over 50 lbs. could be recovered in drillings. This will cause the weight of the standards to be somewhat less than specified, but it seems as though there was no help for it, because to have attempted to make the quantity up from two ingots would have introduced metal of a slightly different carbon, and so brought about an objectionable lack of uniformity.

The metal was turned in a lathe at a very slow speed, and with a blunt tool. The whole time of turning was between three and four months.

In regard to pulverising the drillings as originally proposed, Professor Langley found it utterly impossible to do so by any means which would not introduce a notable quantity of foreign matter. Between chilled rolls the shavings only flattened. They were sifted through a 30-mesh sieve, and the fine material so obtained, which is small in quantity, is in a separate enclosure. The rest of the drillings are as nearly homogeneous as it is possible to make them, because they have been made from "dead melted" stock formed at one heat from a single crucible.

The various Committees are as follows:—Sweden, Professor Richard Akerman, Secretary; Germany, the Government Department of Tests; France, Mons. Ferd. Gautier, Secretary; England, the British Association Committee; United States, three members of the American Society of Civil Engineers, viz., William Metcalf, Thomas Rod, and A. E. Hunt; and three members of the faculty of the University of Michigan, viz., Professors J. W. Langley, A. B. Prescott, and M. E. Cooley.

The material for the standards and the mechanical work on them have been furnished by the Crescent Steel Works of Pittsburgh gratuitously, because of the interest this firm has always shown in promoting the cause of scientific metallurgy.

Professor Langley further says:—"I can make the fifth standard, the 0·08 carbon suggested by your Committee, only it will take probably about two months. I will start upon it in a short time, as soon as I can make the right kind of stock, which will have to be Bessemer, for I can blow a heat as low as that without trouble."

Within the last few days a letter has been received from Professor Langley as representing the University of Michigan, and from Mr. William Metcalf, on behalf of the American Society of Civil Engineers, stating that the samples have been despatched to each of the four countries previously mentioned (Great Britain, France, Germany, and Sweden). It is hoped that the analyses will be commenced almost immediately, and that by the next meeting of the Association the work may be in a forward condition.

Photometry with Nitrogen Iodide.—G. Lion.—The author utilises the decomposition by light of nitrogen iodide prepared by the action of the aqueous solution of pure ammonia at 22° upon iodine. This substance, remaining in the liquid in which it was formed, is slowly decomposed, with an escape of nitrogen proportionate to the intensity of the incident light. He compares the illuminating power of two lights by means of two burettes containing equal quantities of the reagent, and communicating by means of a capillary tube containing a mercurial gauge.—*Comptes Rendus*, Vol. cix., No. 17.

ON WATER ANALYSIS.

By H. M. VERNON.

In Frankland's method of estimating the organic carbon and nitrogen in potable waters by the combustion process, one of the chief difficulties and sources of error seems to occur in the evaporation of the water to dryness. In Frankland's original process of evaporation in a platinum dish on the water-bath, with a covering of filter-paper to keep out the dust and other organic impurity from the air, the evaporation could only be accomplished so slowly that it frequently took two days to evaporate a litre of water to dryness.

We have thus the comparatively unstable nitrogenous organic impurities in the water subjected to a temperature of 100° C. for perhaps fifty hours. It is scarcely possible that some decomposition should not take place under these circumstances. This, indeed, Dr. Frankland admits, and he has even drawn up tables showing the amount of nitrogen lost as ammonia when a water has been evaporated to dryness in the presence of reagents, as phosphorous and sulphurous acids. The amounts given in these tables are to be added to the amount of nitrogen subsequently found by combustion. When the water is evaporated in the presence of sulphurous acid, this amount to be added is about one-fourth of the total quantity of nitrogen found by combustion. When such a large number as this is to be added on to the amount found it is evident that the error in the amount of organic nitrogen really present in the water may be considerable.

These tables mentioned above do not give any information as to the length of time the waters took to evaporate, although this is obviously a very important factor in the determination of the amount of nitrogen to be added on to the amount found by combustion.

It appears that the only way to eliminate these sources of error successfully is to so evaporate the water and obtain the solid residue without the nitrogenous organic constituents in any way undergoing decomposition.

To accomplish this I will mention a very simple method which, I believe, will satisfy these conditions, although I cannot say I have tested it experimentally. It consists simply in evaporating the water under a very small pressure over strong sulphuric acid.

On turning to the tables of the boiling-points of water at various temperatures, it will be seen that water boils at 12° C. under a pressure of 10·457 m.m.; that is, under approximately a pressure of a centimetre. Now, by means of the Sprengel pump it is possible, in a very few minutes, to obtain a pressure far less than this; indeed, with a Sprengel of the ordinary make a pressure of 0·1 m.m. may easily be obtained. If, now, the water to be evaporated be placed in a platinum basin in a desiccator over strong sulphuric acid, and if this desiccator be placed in connection with the Sprengel pump with a vessel of strong sulphuric acid between them to absorb the steam as fast as it is generated, and if the pump be now set in action, so that the pressure in the desiccator is less than 1 c.m., the water in the platinum basin will begin to boil, and will continue to do so until it has evaporated to dryness. By varying the pressure in the desiccator by means of the pump the rate at which the water should boil can be easily adjusted.

In this way, then, it is possible to evaporate the water to dryness without its temperature rising above 12° C., or even less if it be required. It is evident that the nitrogenous organic constituents suffer much less chance of decomposition when the water is evaporated in this way than when it is evaporated at 100° C.; for not only is the temperature of the water never allowed to rise much above 12° C., but also the evaporation takes place in almost total absence of air, and thus again the chances of decomposition of the organic constituents are minimised. A still more cogent argument is, perhaps, the act that by this method the water can be evaporated down in a very few hours, instead of the fifty or so hours required in Dr. Frankland's process. This objection to Frankland's process has, of course, been partly removed by the introduction of Bischoff's method of evaporation.

If the water be evaporated at all fast when the basin is merely placed in the desiccator, such a large amount of heat would become latent, owing to the conversion of water into steam, that in a short time the water would be converted into ice. To obviate this difficulty the evaporation of the water may be carried on in a vessel of glass with double walls. Between these walls a stream of cold water at about the same temperature of the atmosphere is allowed to flow. By this means the temperature of the water in the vessel will never sink low enough for it to freeze, and if the stream of water circulating between the walls be at all rapid it will not sink to more than a degree or so lower than the temperature of the water surrounding it.

It will simplify matters if this double-walled evaporating basin is itself made to answer the purpose of a desiccator, and thus to render unnecessary the use of the ordinary form of desiccator. All that is necessary to render this possible is that the evaporating basin should have a broad rim ground smooth; a glass lid, also ground smooth on its under side, is fitted to this, so that an air-tight connection is obtained. In the lid it will be necessary to have a glass stopcock connected with the Sprengel, so that the required pressure may be obtained.

As the quantity of water required to be evaporated would probably be considerable, and it would be inconvenient to have an evaporating basin of the above form large enough to hold it all at once, another hole is made through the lid, and through this projects the end of the tube of a tap funnel. The tube must be fitted into the lid, so that an air-tight connection is obtained. This may be effected either by fitting a caoutchouc cork in the hole and passing the end of the tube through this, or by grinding down both the tube and the hole, so that the one fits accurately into the other. If the stoppered funnel is chosen of such a size that it holds exactly half a litre when filled up to a mark in the neck, it will be easy to evaporate down a half litre or a litre of the water, as the case may be, without any further trouble of measuring.

It will be found more convenient to have the tube of the funnel long and to have two glass taps in it a few inches apart than to have only one tap. The reason of this will be made obvious.

The pressure of the atmosphere is about 760 m.m., while that inside the vessel is only about 10 m.m. If, now, supposing the funnel only had one tap, this tap were opened, this comparatively large pressure upon the water in it would drive the water with considerable force into the evaporating basin, so that probably some of it would be carried over mechanically into the vessel of sulphuric acid used for absorbing the steam from the water, and thus some of the residue would be lost; also, more of the water may enter the basin than it would be convenient to evaporate at a time. If, now, two taps are used instead of one, this difficulty is entirely obviated. Thus, to introduce the water into the evaporating vessel by this means the upper tap is first opened, the lower one being closed; the water runs down the tube and fills the space between the two taps; the upper tap is then closed and the lower one opened; the pressure in the evaporating basin being almost nil, the column of water between the two taps will run down into the evaporating basin and there be evaporated. We have thus introduced a small definite volume of the water into the evaporating vessel without danger of any loss of organic matter, owing to some of the water being carried over mechanically into the vessel containing the sulphuric acid.

In this way, the whole of the water is introduced in small quantities from the funnel into the evaporating vessel, and is there evaporated.

The vessel of sulphuric acid here spoken of is placed between the tube leading from the evaporating vessel and

the Sprengel pump; its purpose is to absorb the steam distilling over from the water as it evaporates. In order that this water may distil over without trouble, the vessel of sulphuric acid should be surrounded by another vessel containing water at a few degrees lower temperature than the water circulating between the walls of the evaporating basin. The quantity of sulphuric acid in the vessel should be considerable, as it has to absorb half a litre or a litre of water.

During the whole of the evaporation the Sprengel must be kept at work; if it were not, the pressure in the evaporating vessel would soon rise, and the water cease to boil; this being due to the escape of the gases dissolved in the water.

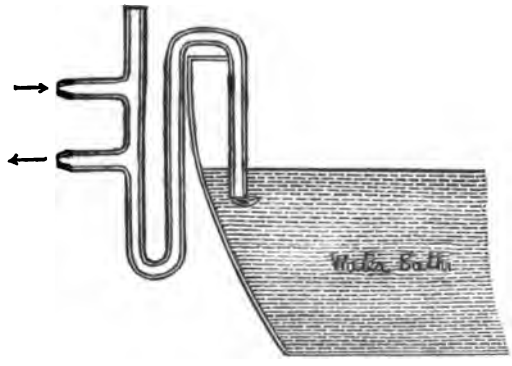
If the residue left after evaporation is required to be weighed, it must be scraped out of the evaporating basin into a weighed platinum basin, and then weighed. A better plan would be employ, during the whole process of evaporation and subsequent weighing, a weighed platinum vessel of the same shape as the interior of the evaporating vessel, and fitting tightly in it. At the end of the evaporation it could be removed from the evaporating basin and weighed.

It must be remembered that this method of evaporation is, so far, entirely theoretical, as I have not myself at present the means for testing it experimentally; it is brought forward merely as a suggestion, and it is hoped that it will be received as such.

A SIMPLE WATER-BATH REGULATOR.

By T. H. EASTERFIELD, B.A., F.C.S.

THE apparatus represented by the accompanying figure is a simple and effective arrangement for keeping the water in water-baths at constant level. The idea is possibly old, but seems unknown in the laboratories with which I am acquainted.

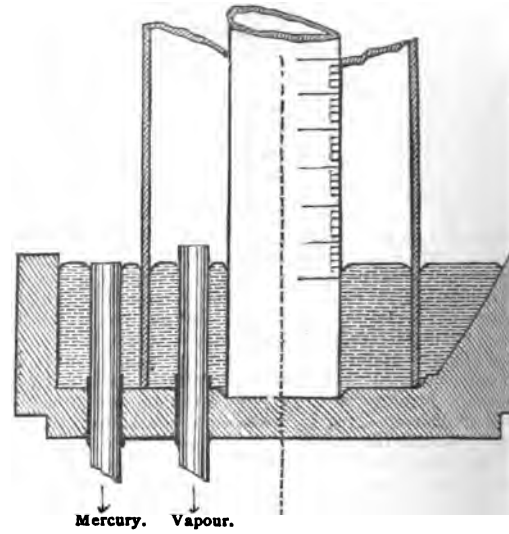


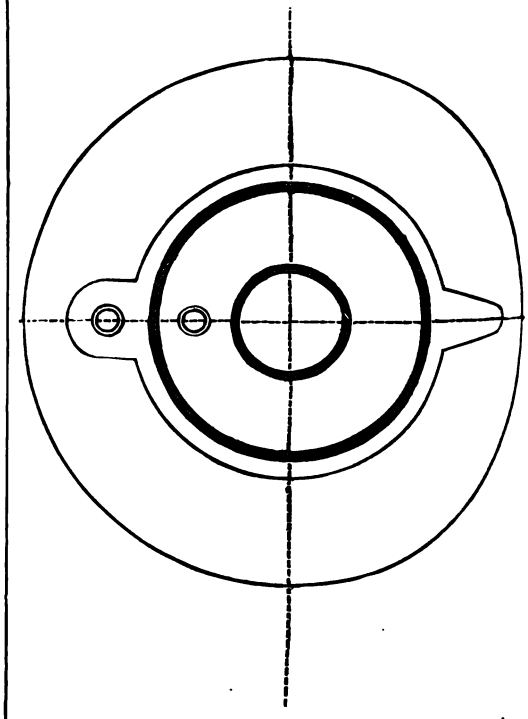
The arrangement consists of a piece of glass tube, open at each end, bent twice, parallel to itself, and having two side-tubes sealed into the longest limb. The upper side-tube admits the water supply, the lower is the overflow-pipe. When the tube has once been filled with water, by turning on the water supply and stopping the overflow-pipe for a moment, the instrument acts as a continuous syphon, keeping the water-level constant.

A HANDY TROUGH FOR HOFMANN'S VAPOUR-DENSITY APPARATUS.

By T. H. EASTERFIELD, B.A., F.C.S.

THE accompanying figure represents a cheap and effective trough for use in determining vapour density by Hofmann's method. It consists of a thick disc of wood turned to fit tightly into the ring of an ordinary retort stand, and hollowed out in the manner shown in the section. Through the bottom of the trough pass two glass tubes, kept in place by bits of rubber tubing. One of these glass tubes lies outside the steam-jacket, and serves for the escape of the mercury, which runs away, clean and dry, into a bottle placed to receive it. The second tube passes into the steam-jacket and leads away the steam and condensed water.





The trough is, of course, made to just fit any particular size of steam-jacket, and should be just large enough to allow the operator to work conveniently. The arrangement ensures that the lower level of the mercury shall be approximately constant; very little mercury is required, and that which runs away is perfectly clean.

The apparatus has been tried for two years in the

Cambridge University Chemical Laboratory, and also in the Würzburg Physical Laboratory, and has given great satisfaction.

NEW OBSERVATIONS ON THE RECIPROCAL DISPLACEMENTS BETWEEN OXYGEN AND THE HALOGENS.

By M. BERTHELOT.

The author has indicated how the reciprocal displacements between oxygen, on the one hand, and, on the other hand, the halogens, chlorine, bromine, iodine, combined either with metals or non-metals, or with hydrogen, are foreseen by the thermo-chemical theory, and verified exactly by experiment, and he has lately extended these relations to fluorine. He now purposes explaining the interpretation of various reactions of the same order, more delicate, and effected at the ordinary temperature, commencing with hydrochloric acid.

The formation of dilute hydrochloric acid from its elements (H+Cl) liberates +39·3 cals., whilst that of liquid water (H + O) liberates only 34·5 cals. Hence oxygen does not decompose dilute hydrochloric acid in the cold, whilst chlorine decomposes water at the ordinary temperature, with the simultaneous formation of the oxy-acids of chlorine, as theory indicates. But hydrochloric acid gas possesses, on the contrary, a formation-heat of +22 cals., lower than that of gaseous water (+29·5 cals.), at least at ordinary temperatures, for at 2000 the two quantities become equal, and at still higher temperatures the formation-heat of hydrochloric acid gas predominates. Hence various reactions and equilibria, which have been studied elsewhere ("Essai de Mécanique Chimique, ii., p. 500). Theory indicates that these equilibria may be manifested at ordinary temperatures on operating suitably, for instance, with fuming hydrochloric acid, which is a mixture of various hydrates with the anhydrous acid. Still it has not been found that this acid, when perfectly pure, undergoes any decomposition in the cold, even if exposed to a moderate solar light.

It has been found that the reaction in the cold may be determined by adding to the hydrochloric acid certain metallic chlorides, the influence of which, assimilable to what was known of old as actions of contact, results in reality in the formation of intermediate compounds, which serve as steps towards the completion of the reaction. Such, in particular, is manganous chloride. After placing, in a large flask full of air, about 20 c.c. of very pure fuming hydrochloric acid, the flask has been exposed for several weeks to the sun without either the air or the liquid acquiring the odour of chlorine, or the power of decolourising a dilute solution of indigo. But if there are added to the liquid a few decigrms. of pure manganous chloride, it gradually becomes coloured, even in diffused light, or better in the sunlight, and it acquires the brown tint of the compound which precedes the formation of chlorine in its preparation by the action of hydrochloric acid and manganese peroxide, or, it might be said, the hydrochlorate of manganese peroxide which has been described in the *Annales de Chimie et Physique*, Ser. 5, vol. xxii., p. 464. This tint augments for several days, up to a certain limit. At the same time the air above is charged with gaseous chlorine and the liquid below acquires bleaching properties.

This formation of chlorine results from the absorption of ordinary oxygen by the liquid, and from the dissociation of manganese perchloride hydrochlorate, formed in consequence of this absorption, and of the presence of an excess of hydracid not saturated with water. If the chlorine in the air above is eliminated and replaced by hydrochloric acid mixed with oxygen, the phenomenon is reproduced, and it is clear that it may be reproduced indefinitely by reason of a known mechanism of dissociation, which incessantly regenerates a new dose of free chlorine, of hydrochloric acid, and of manganous chloride. But if we do not introduce hydrochloric acid the reaction will stop about the point where there only exist hydrochloric hydrates saturated with water, such that the gas no longer possesses any appreciable tension. In fact, the author has found that hydrochloric acid diluted with water, and not fuming, is no longer decomposed by oxygen, even in presence of manganous chloride.

Manganous chloride is especially apt to produce these phenomena. With ferric chloride added to fuming hydrochloric acid we obtain signs of reaction, but almost insensible and difficult to show.

Reactions of the same order intervening equally, with formation of dissociated intermediate compounds, occasion the displacement of the chlorine in hydrochloric acid by the oxygen of the air, and latterly it has been industrially utilised on the large scale.

We see, by these observations, how energies in some sort latent, and capable, in principle, of producing exothermic phenomena, but which, in fact, do not produce them under given conditions, may be rendered manifest by the intervention of certain agents acting only as intermediate stages, and capable of developing indefinite reactions. Here is the whole thermo-chemical theory of action of presence.—*Comptes Rendus*, cix., No. 15, p. 546.

ON COMMERCIAL QUERBRACHO EXTRACT AND ITS DETECTION.

By J. A. WILSON.

It occurred some time since to the writer that the presence of certain alkaloids in querbracho might prove of advantage in detecting the extract from that wood in dyewood extracts, such as logwood, berry, fustic, &c. On page 99 of Allen ("Commercial Organic Analysis," vol. iii.), *Aspidospernum Querbracho* is mentioned as the source of the commercial extract, but I am informed that Querbracho Colorado is the one most generally used.

Commercial querbracho extract is said to be mixed with other astringent drugs, and palmed off as extract of querbracho, so that if the presence of the alkaloids were proved in the genuine extract, the amount in these doctored extracts would be very variable. However, I determined to see whether any alkaloids could be obtained from the commercial extract, as manufactured by first class firms, and two samples were therefore examined in the same manner as used for detection of glucosides and alkaloids in general. Sample No. 1 gave me:—

1·86 per cent ash (0·81 soluble, 1·03 insoluble). Alkalinity of soluble equal 0·37 per cent K_2O.

30·47 per cent total non-volatile solids.

The total solids on extraction gave—

3·2 per cent petroleum ether extract.
50·7 „ alcoholic extract.

Fifty grms. of the extract was examined for alkaloids in the following manner:—

1. Evaporation in a vacuum at 50° C.

2. Residue treated with 150 c.c. of 90 per cent alcohol acidulated for eighteen hours.

3. Treating the residue obtained on evaporation of alcohol with six times the volume of water for twelve hours and filtering.

4. Treating the filtered liquid from 3 with immiscible solvent, petroleum ether, benzol, chloroform, &c., in the acid state.

5. The liquid, after extraction in the acid state, is rendered strongly alkaline with ammonia, and extracted as before with petroleum ether, benzol, and chloroform; the latter quite warm.

The residues obtained on evaporation and recovery of solvent were then examined by the general group reagents, and by the sulphuric acid and lead peroxide test, also by sublimation.

I may say that I failed to detect the least trace of any alkaloid whatever.

The Laboratory,
Tottington, near Bury.

PURIFICATION OF HYDROFLUORIC ACID FOR USE IN ANALYSIS OF SILICATES, &c.

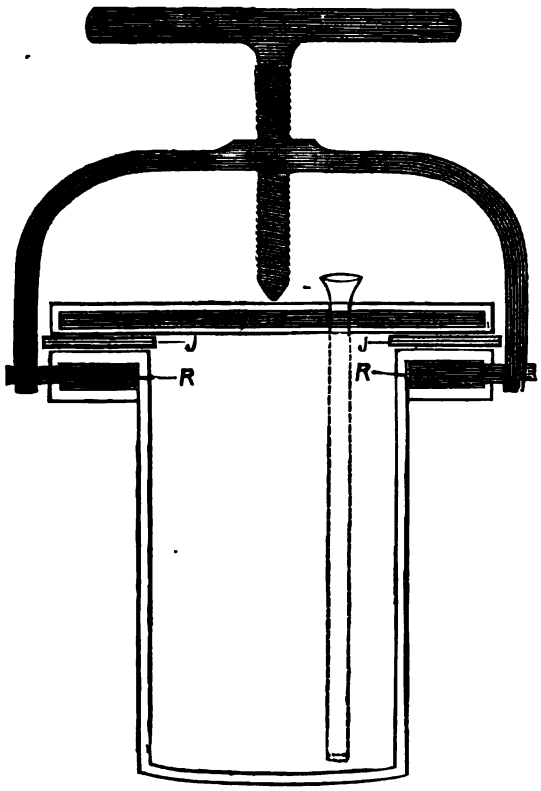
By ROBERT HAMILTON, F.I.C.

HAVING for two years used the process for the analysis of silicates almost as described by George Craig (CHEMICAL NEWS, lx., 227), I can testify to its usefulness, speed, and even elegance; its accuracy has been long established.

FIG. 1.

Arrangement of Nose of Retort for Distilling Hydrofluoric Acid.

FIG. 2.



Leaden Retort for Distilling Hydrofluoric Acid.
R, Wrought iron ring, 1 in. × ⅛ in.; J, India-rubber ring joint.

The leaden retort adapted by me to the distillation of the commercial hydrofluoric acid fulfils its purpose extremely well, and I submit a sketch of it in the hope of facilitating the adoption of the process.

The body of the retort is 6 inches high by 4 in diameter, of heavy sheet-lead, and a broad seat is formed for the sheet india-rubber joint, J, by beating the lead back over an iron ring, R, 1 inch wide by ⅛-inch thick. Two projections, from opposite sides of the ring serve to secure the ends of the iron bridge (1 inch wide by ⅛-inch thick), which is the main feature of the retort. The lid is made of ¼ inch iron plate covered with lighter sheet lead. All the lead joints are burned.

The remainder of the sketch is self-explanatory. It will be observed that the leaden nose of the retort points upwards, and that the india-rubber tube is carried a little higher, to ensure that no dissolved lead is carried down.

For condenser, I use thin-walled black india-rubber tubing, of $\frac{3}{16}$-inch bore, connected to the leaden nose by stouter tubing of larger bore, and passing through india-rubber corks in ends of Liebig's condenser case. The crude strong acid rapidly attacks and destroys the india-rubber tubing, and should be diluted till it contains about 25 per cent HF, when an acid comes over of very convenient strength for analytical work.

After charging the retort, I heat it in the stink-box, attach a short piece of india-rubber tubing to the nose, and at frequent intervals place the free end of the tube in water, till silica (of which there is usually a little) ceases to separate. The retort is then transferred to the condenser, and, after a little regulation of the heat, the distillation proceeds quietly and smoothly, and becomes one of the easist of laboratory operations.

Flocks of sulphur, which sometimes separate, may be removed by letting the distillate filter through paper, in a vulcanite funnel, into the india-rubber receiver.

Eglinton Iron Works,
Ayrshire, N.B.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, November 9th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, the whole were found to be clear, bright, and well filtered.

Throughout the past month of October the supply of water to the Metropolis has continued to be of excellent and very uniform character, the proportion of organic carbon in any single sample of Thames-derived water

examined varying only from 0·135 to 0·155 part in 100,000 parts of the water; with a mean of 0·143 part, as against a mean of 0·138 part in the previous month's supply,—the absolute difference of 0·005 part in 100,000 parts of the water being wholly insignificant.

In respect also to its clearness, its degree of freedom from colour-tint, and its minute proportion of matter oxidisable by permanganate, the October water supply has well sustained the satisfactory character presented by the supply of the previous month.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Burgess, 7, Wellington Road, Peckham; William Frederick Britcher, 33, Tranquil Vale, Blackheath; Frank Hill Perry Coste, Ravenshoe, Burnt Ash Hill, S.E.; David Brown Dott, 104, South Canongate, Edinburgh; Robert Stephen Edwards, B.A., Gwern-y-Gaseg, Minera, Wrexham; James Kerr Erskine, 6, Lascotts Road, Wood Green, N.; John Foggie, Newport, Fifeshire, N.B.; Harold Gripper, 77, Cecil Street, Greenhays, Manchester; H. B. Helbing, German Hospital, Dalston; Robert Edward Hughes, 15, Clare Street, Canton, Cardiff; James Robert Kaye, 33, Great Charles Street, Birmingham; Henry Richard Kerwood, M.B., Frogmore Broadelyst, Devonshire; Frederick Thomas Knott, The Laurels, Eltham Road, Lee, Kent; L. Napier Levingham, Brightside Steel Works, Sheffield; G. B. Mason, Barbados, West Indies; James Braik Mason, 3, Park Terrace, Dundee; Thomas Mercer, Great Hey, Edersfield, near Bury, Lancashire; Joseph Alfred Nettleton, East Grinstead, Sussex; Wallace Christopher Nickels, 14, Yew Grove, Cricklewood, N.W.; James Gordon Parker, Penketh, near Warrington; Alfred Edridge Pike, Westminster Medical School, S.W.; William Ping, 2, Sandbourne Road, Brockley, S.E.; Frederick Quincke, Ph.D., 13, Portland Terrace, Regent's Park, N.W.; Sydney Augustus Sworn, 3, Peel Street, Bedford; Willis G. Tucker, M.D., Albany, N.J., U.S.A.; Daniel Walker, School of Mines, Ballarat, Victoria; Matthew Whittam, St. Peter's School, York; Basil P. Wigan, Macclesfield; John Wilkie, 20, Buckingham Street, Charing Cross; John Wiltshire, Knowsley Cottage, Torre Park, Torquay.

The following papers were read:—

87. "*Isolation of a Tetrahydrate of Sulphuric Acid Existing in Solution.*" By S. U. Pickering.

The freezing-points of mixtures of sulphuric acid and water form three distinct curves, representing the crystallisation of water, of $H_2SO_4 \cdot H_2O$ and of sulphuric acid respectively; in each of them the highest point is in exact correspondence with the composition of the substance which crystallises out. No solutions containing between 75 and 40 per cent of acid had yet been frozen, but it appeared to the author that if his former deductions from the irregularities in the curves representing the densities and other properties of solutions of the acid were correct, an independent curve representing the crystallisation of a new hydrate should occupy this interval, and that this new hydrate could only be either $H_2SO_4 5H_2O$ or $H_2SO_4 4H_2O$. Experiment has proved that it is the latter. The two branches of the new curve obtained rise from about −8°, and meet in a sharply marked angle at a point exactly corresponding to the composition of the tetrahydrate, the temperature at which this point is reached being −25°. The tetrahydrate forms large, well-defined, hard crystals.

Apart from the consideration that the isolation of this hydrate was the direct outcome of his having previously recognised its existence in the dissolved state, the author maintains that the crystallisation of a substance from a liquid necessitates the recognition of its existence in that liquid. The various possibilities are (1) that the solid constituents solidify separately in the proper proportions, and subsequently combine: this view is obviously untenable; (2) that the molecular aggregates constituting the solid are formed directly from the acid and water: this means that a hydrate has no fundamental molecule, and, besides, leaves the impossibility of explaining how these solid aggregates can hunt each other out, and congregate to form large crystals; (3) that fundamental molecules of the hydrate are formed in solution, but cannot remain there, and consequently separate out almost immediately: this is tantamount to saying that the hydrate is an insoluble substance, a proposition which could scarcely be maintained even if the substance were not crystalline; (4) that the molecules of the hydrate are formed in the liquid, and exist there till the temperature is lowered below its freezing-point. This, in the author's opinion, is the only tenable hypothesis.

When a liquid freezes and melts at a definite temperature, when the temperature remains constant till the whole of the liquid is frozen, when any alteration in its composition lowers its freezing-point, we have the most certain evidence yet adduced for regarding that liquid to be a definite, though, possibly, somewhat dissociated, compound. If we deny this argument as applied to the hydrate in question, we must deny it in all cases, and conclude that no liquid is a definite substance.

The author does not argue that the mere fact of the existence of the liquid hydrate at −25° implies its existence at the higher temperatures (8—38°) at which his density and other determinations were made; on the contrary, he argued that because it existed at the higher temperatures it must exist at the lower ones, and having proved this to be a fact he holds that the premisses from which his conclusions were drawn must be correct.

The author believes that the dihydrate may yet be obtained as a solid, since there is a reach of 7 per cent in its vicinity where freezing-points have not yet been attained. He has also isolated another hydrate which crystallises in small quantities with the monohydrate, but has not succeeded in determining its composition.

88. "*Additional Observations on the Magnetic Rotation of Nitric Acid and of Hydrogen and Ammonium Chlorides, Bromides, and Iodides in Solution.*" By W. H. Perkin, Ph.D., F.R.S.

In his previous experiments (*cf.*, *Proc. Chem. Soc.*, 1889, p. 83), the author had limited his observations on nitric acid to the pure acid, HNO_3; he has now examined a somewhat diluted acid, and the results obtained indicate that HNO_3 unites with water, forming an acid analogous to orthophosphoric acid, viz., $(HO)_3NO$.

The experiments on hydrogen chloride, bromide, and iodide were originally made on single samples in a very concentrated solution of each. These gave abnormally high results—rather more than twice the values calculated for the pure compounds—but on examining solutions of different strength it was found that the rotation *increases* up to a dilution equivalent to about 6 or 7 mols. of water to 1 mol. of hydride, the value then remaining practically stationary. To see whether the solvent had any influence, a solution of hydrogen chloride in isoamyl oxide was examined, and was found to give values nearly identical with those calculated from the chlorine derivatives of the paraffins; and there can be little doubt that if

the other hydrides could be examined in a similar way analogous results would be obtained. As union with water should reduce the rotations, the results at present are quite inexplicable.

The compounds with ammonia and the compound ammonias have been also further examined; the results are remarkable when considered in relation to those afforded by the hydrides, as the rotations found, instead of being those calculated from the results obtained in the case of paraffin-derivatives, or those *found* in the case of hydrogen chloride dissolved in isoamyl oxide, nearly correspond to those required on the assumption that the hydrides are present in aqueous solution together with ammonia. The rotations, however, do not vary with the strength of the saline solutions. The author's explanation of this is that when the salts are dissolved in water they dissociate almost entirely into the hydride and the amine, the hydride undergoing an increased rotation on account of its being in aqueous solution. In the case of triethylamine chlorhydride the numbers are lower, and there is evidently less dissociation; and in the case of tetrethylammonium chloride little or no dissociation appears to take place. Solutions of ammonium iodide and diethylamine chlorhydride in absolute alcohol gave somewhat lower numbers than aqueous solutions, indicating a somewhat smaller although large amount of dissociation.

As already noticed, ammonium nitrate gives numbers very close to the calculated; apparently it does not dissociate to any appreciable extent. As the author was not satisfied with the numbers obtained for neutral ammonium sulphate, the acid sulphate was examined, and this gave the calculated numbers; these, when compared with those for the neutral salt, show that the latter undergoes dissociation to a small extent when in solution, which is in agreement with the well-known fact that its solution in water gives off ammonia when heated. The examination of these oxy-salts shows clearly that the salts containing hydrogen chloride, bromide, and iodide, when in aqueous solution, are in a very abnormal condition, but a condition which is easily explained if they are in a state of dissociation.

Discussion.

Dr. Gladstone said that when the refraction equivalents of the hydrides of the halogen elements and of nitric and sulphuric acids in solution were first determined, it was observed that the values were far higher than those calculated; but on re-examining hydrogen chloride solutions he had recently found that as the amount of water was increased a slight increase in the specific refraction also set in quite analogous to that described by Dr. Perkin. The whole subject of the behaviour of such substances in solution deserved a full and deliberate investigation with reference especially to the possible occurrence of dissociation. He had little doubt that some dissociation did occur in the case of the ammonium salts. As it is well known that increase of temperature greatly promotes dissociation, it would be well to repeat the observations at various temperatures in order to learn whether a change takes place in the refraction and magnetic rotation. On examining Dr. Perkin's solution of hydrogen chloride in amyl oxide, he found that the refraction and dispersion values deduced for the chloride are very much smaller than those afforded by aqueous solutions: thus another case of correspondence between the three properties of magnetic rotation, refraction, and dispersion of light was made evident.

Professor Ramsay, referring to the high values observed by Dr. Perkin in the case of dilute solutions, drew attention to recent speculations concerning the occurrence of atomic dissociation in solutions, and asked, might not the high values be explained by assuming that hydrogen chloride underwent dissociation into hydrogen and chlorine atoms?

Dr. Armstrong said that although it might be argued from the results obtained with aqueous solutions, that atomic dissociation attended dilution, the fact that norma values were obtained when amyl oxide was used as solvent was evidence of the insufficiency of such an explanation, and clearly indicated that the water played an active part; according to the now fashionable dissociation hypothesis, the solvent acted merely as a diluent, as one gas does to another, dilution corresponding to reduction of pressure; on this hypothesis, therefore, the values obtained should be the same for solutions of equivalent strength in either solvent. Dr. Perkin's results appeared to indicate that a certain proportion of the water molecules —those which were carried round, as it were, by the hydrogen chloride molecules — underwent what might be termed *extra* rotation. Dr. Perkin based his conclusion that hydrates would afford lower and not higher values on the results which he had obtained in the case of compounds such as the hydrates of nitric and sulphuric acids, and of aldehyd, and of chloral; but these were all hydrates of compounds containing polyad elements; the behaviour of monad elements might well be peculiar. In fact, in discussing these questions, valency must be taken carefully into consideration. Dr. Gladstone had suggested that observations should be made at various temperatures; such observations would undoubtedly be of importance, and might even be expected to afford a final settlement in favour of one or the other hypothesis. If the increased rotation be conditioned by hydrates, as such hydrates would undergo dissociation on heating, the values would diminish as temperature rose; but if atomic dissociation took place, the change would be in the contrary direction, although, as the effect of temperature in promoting atomic dissociation is often not very marked until a somewhat higher temperature is attained, the effect of moderate heating would not necessarily be exhibited by an increase of the rotation.

89. "*Phosphoral Trifluoride.*" By T. E. Thorpe, F.R.S., and F. J. Hambly.

The authors find that phosphorus oxyfluoride, POF_3, may be easily and conveniently made by heating a mixture of cryolite ane phosphoric oxide, and collecting the products at the mercurial trough. The interaction appears to be strictly analogous to that by which Kolbe and Lautemann obtained phosphorus oxychloride by heating phosphoric anhydride with common salt;—

$$2P_2O_5 + 3NaCl = POCl_3 + 3NaPO_3$$

(*Ann. Chem. Pharm.*, cxiii., 240).

90. "*Acetylation of Cellulose.*" By C. F. Cross and E. J. Bevan.

By heating cotton cellulose with acetic anhydride and zinc chloride (Franchimont, *Ber.*, xii., 2059) the authors have obtained a product which, judging from the results of analysis and the proportion of acetic acid which it yields when submitted to alkaline hydrolysis, appears to be a *pentacetyl* derivative of cellulose; the yield was found to be 83 per cent of that calculated for a pentacetate, and the insoluble product of hydrolysis exhibited the behaviour of a normal cellulose. The compound is very stable, being re-precipitated unchanged from its solution in a mixture of nitric and sulphuric acids. It would appear, therefore, that all the oxygen of the cellulose molecule acts as hydroxylic oxygen. In discussing the bearing of these results, it is pointed out that the evidence upon which substitution of OH in the cellulose molecule has been assumed to be at a maximum with the triacetate (Schutzenberger) and trinitrate, is insufficient. Franchimont's representation of the molecule of cellulose as an aggregate of "glucose" groups, condensed according to the equation $n(C_6H_{12}O_6) - (n-1)H_2O$ (R.T.C., ii., 241), is based upon strong evidence, but affords no suggestion of the mode in which the condensation takes place. The extreme inertness of cellulose, as evidenced by the fact that it does not interact with acetic anhydride at its boiling-point, but only at a temperature of 180°; its resistance to the powerfully hydrolytic action of acid sul-

phites at high temperatures; together with the results detailed in this communication, go to show that it is probable that cellulose represents a type of carbon compound *sui generis*.

DISCUSSION.

Dr. ARMSTRONG remarked that present ideas as to the constitution of cellulose are mainly an extension of our views concerning carbo-hydrates of the cane-sugar and dextrin groups: we are accustomed to regard these latter as etheric-derivatives of the glucoses and to look on cellulose as a compound of a somewhat similar type; but its physical properties, its behaviour on acetylation, and the peculiar condition under which alone it undergoes hydrolysis, serve to indicate that perhaps it is a compound of a different and special type, as the authors of the paper suggest may be the case. In seeking to formulate the constitution of cellulose, the possibility that it may even be a closed chain compound should not be entirely overlooked, the occurrence of compounds such as inosite and quinic acid—both derivatives of hexhydrobenzene—in plants being not without significance from this point of view.

91. "*Action of Light on Moist Oxygen.*" By ARTHUR RICHARDSON.

The author finds that the presence of liquid water very much facilitates the oxidation of many substances under the combined influence of sunlight and oxygen. If, however, the water is present as aqueous vapour, the decomposition is exceedingly slow, and in some cases is entirely arrested.

He finds that peroxide of hydrogen is formed when water containing pure ether is exposed to light in an atmosphere of oxygen; on shaking some of the ether with a solution of potassium bichromate, the ether at once assumed a decided blue colour.

From an extended series of experiments the following facts have been observed:—(1). The amount of hydrogen dioxide formed depends on the proportion of ether to water present. (2). No dioxide is formed when a mixture of water-vapour, ether-vapour, and oxygen is exposed to sunlight. (3). No dioxide is formed when water and ether are exposed in an atmosphere of carbon dioxide. (4). No iodine is liberated from potassium iodide by a mixture of water, ether, and oxygen from which light has been excluded.

On exposing pure water, acidified with pure sulphuric acid, to light, hydrogen dioxide was found in the solution; this was estimated by permanganate of potassium. Water exposed to rays of low refrangibility gave no hydrogen dioxide.

On placing water which contained the dioxide, immediately after exposure to light, in the dark, it was found, after some time, to be free from dioxide; but hydrogen dioxide was formed on again exposing the solution to light; this process could be repeated indefinitely.

From these and other experiments the author is led to believe that the oxidation of substances under the influence of light involves in many cases initially an oxidation of water to hydrogen dioxide, and that the oxidation of the compound is the result of a secondary interaction between it and the hydrogen dioxide.

DISCUSSION.

Dr. ARMSTRONG said that it had long since been stated that peroxide of hydrogen was formed when ether and water was exposed to atmospheric oxidation; Mr. Kingzett had brought the subject under the notice of the Society several years ago (*cf. Chem. Soc. Journ.*, Abstr., 1877, p. 183). Dr. Richardson assumed that the water was directly oxidised; Mr. Kingzett had argued—and in the case of turpentine had adduced weighty experimental evidence—that the hydrogen peroxide was a secondary product, formed by the action of water on an organic peroxide. It was impossible to say from Dr. Richardson's results which explanation was the correct one; perhaps neither was wholly correct, as it was not impossible that the conjoint influence of the water and ether was an essential feature of the interchange with oxygen. Dr. Richardson had added ether or sulphuric acid with the object of protecting the peroxide from decomposition; surely weak solutions of hydrogen peroxide were not so unstable that proof could not be obtained of its formation if it really were produced on exposing water and oxygen to light. There was no satisfactory evidence that it was formed in the absence of a third substance. In the case of the experiments made without ether, it was just possible that the minute amount of organic matter present in the water—perhaps that derived from stoppers—had been effective in promoting peroxidation; the disappearance of the peroxide in the dark tended to favour this view.

Professor THORPE said that he had recently had occasion to satisfy himself that water played an important part in promoting peroxidation. It had long been known that the atmospheric so-called ozone reactions were at least principally due to hydrogen peroxide; finding in the Admiralty instructions the statement that the air of the Hebrides was said to contain more ozone than any air in the world, he had, during a recent yachting tour there, exposed Schönbein paper at various distances above sea level; he had always found that, after six hours' exposure the "ozone" manifestations were very much stronger five or six feet above the sea than some distance above the sea, at the mast-head of the yacht.

Professor RAMSAY drew attention to the fact that when a substance capable of destroying hydrogen dioxide was present, the peroxide might be formed and immediately thereafter destroyed. Such was probably the case in polluted rivers; and it might well be that the continual formation and decomposition of hydrogen peroxide was the effective cause of the oxidation of organic matters in waters. Its formation apparently tended towards a maximum, which, in presence of matter capable of decomposing it, would never be reached (*cf.*, *Proc. Chem. Soc.*, 1886, p. 225).

Mr. GROVES remarked that weak solutions of hydrogen peroxide were by no means unstable, but would keep for months.

Professor DUNSTAN asked whether Dr. Richardson had proved that the oxidising substance was hydrogen peroxide. He had made a series of experiments which showed that it was not formed when *pure* ether was used, although a substance was produced which was capable of liberating iodine.

Dr. THORNE, referring to the possible effect of a third substance in influencing oxidation, said that he had had occasion to observe that in bleaching coloured fibres a solution of 75 per cent strength of hypochlorite in presence of oxygen gave the same results as one of 100 per cent strength used alone.

The question was asked whether the precaution had been taken in the experiments with potassium iodide to exclude carbon dioxide from the air.

The PRESIDENT said that in experiments which he and Captain Abney had made together on the fading of water-colours, the action of aqueous vapour had been most strikingly apparent; colours were found to be stable on exposure to light in dry air, which were considerably affected when aqueous vapour was present.

Dr. RICHARDSON, replying, said that the bichromate test indicated that the substance formed in presence of ether was hydrogen peroxide. Using pure water, he had obtained traces of peroxide, which, however, could not be estimated. In some cases the bottles in which the exposure to light was effected were provided with glass stoppers. He thought that very little was known as to what happens when iodine separates from potassium iodide: the solution does not exhibit an alkaline reaction.

(To be continued).

NOTICES OF BOOKS.

Chemical and Physical Studies on the Metamorphism of Rocks. Based on a Thesis with Appendices written for the Doctorate in Science in the University of London. By A. Irving, D.Sc., B.A., F.G.S. London: Longmans, Green, and Co.

Geology has of late years undergone a transformation approximating to that which has been witnessed in biology, and of a similar nature. In the hands of Dr. Irving and of like-minded investigators it is being elaborated on that grand principle of evolution which is re-animating all the sciences.

We hope it will not be considered an unpardonable digression if we notice the very advanced views regarding higher education which the author puts forward in his preface. He writes:—"The departure which our University (London) has now made in recognising original work and in doing its part in lifting the discussion of higher scientific questions out of the professional arena . . . . augurs well for the future of science in this country. It may be questioned whether the outcry referred to (that against cram and examinationism?) is not, to a great extent, a reflex of a belief in that system of over-teaching which has done so much to check the growth of original scientific thought in this country, as compared with some of the leading nations of the civilised world, by giving too much advantage in the academical race to mere receptivity." Most true; but is it not a radical error to make the academical career a "race"? The author proceeds:—"It seems to be forgotten at times that the truest 'teaching' is that which stimulates the mind to active thought, not that which saves the student the trouble of thinking by loading the memory with second-hand knowledge. One necessary consequence of this is seen in the rareness of appeals in a great deal of the scientific literature of this country directly to nature as compared with the quotation of names of authority as giving weight to certain views." He continues, more questionably:—"There are reasons for doubting whether, with the exception of the Royal Society, there is a single scientific society in London which is entirely free from the interested influence of a close profession." We think such societies can be found, because some such bodies are not built on lines coinciding with the limits or the interests of any profession.

But we must unhesitatingly agree with Dr. Irving when he says:—"Those on the other hand to whom it has been given to experience the regenerating influence of Nature upon the human intellect will acquit me of any suspicion of cant when I say that above and beyond any honours which it is in the power of any academical body to bestow, nay even beyond and above the appreciation of one's work by one's own contemporaries, research confers its own reward in the healthy habit of mind which it induces."

Turning to the body of the work we find, after some preliminary explanations, in which the author complains very justifiably of the vagueness of existing nomenclature, a discussion of paramorphism, or mineral change, of metatrophy, or changes in the physical characters of rock-mass, and of metataxis, or changes of order of the constituents of the rock-mass. He criticises such utterances as that of Mr. Green, that, according to his (the author's) theory "the constituents of those rocks (the archean crystalline schists) were supposed to have been held in solution in an ocean of boiling water, and to have been deposited as it cooled." He considers that any geological argument which "proceeds on chemical and physical lines" is, in some quarters, unduly depreciated.

In treating of the metataxic work done by solar and lunar tides, the author objects to one of the results put forward by Prof. R. S. Ball. That eminent astronomer concludes that some millions of years years ago the tidal wave must have been several hundred feet high. This might be granted if we assume that the quantity of water condensed on the globe was the same as it is now. But the author tells us that this, on Prof. Ball's own showing, we have no right to do. He quotes Zoellner's view of five successive stages in the life of worlds: (1) the nebulous phase (condition of glowing gas); (2) the glowing liquid phase, as in fixed stars with constant brilliancy; (3) development of a solid glowing crust, as in fixed stars of variable brilliancy; (4) bursting of the thin crust and extensive eruption of the glowing fluid interior; (5) the gradual thickening of the solid crust and condensation of water upon it.

On our globe this last stage must be the Cambrian era. In connection with this subject we note a remark which will be welcome to judicious workers in every branch of science:—"It must be recollected that the output of the mathematical mill will depend upon what is put into it." If we put in visions the result will be dreams.

In his conclusions the author insists that it is a vain and useless task to think of finding any one principle of metamorphism. He thinks it evident that the earth must have, in the course of its development, passed through a *pre-oceanic* stage. He regards the archean series of rocks as representing, upon the whole, the primordial earth's crust, from which the siliceous materials of the sedimentary rocks have been for the most part derived, and considers that "one more chapter is thus added to the history of that great Law of Evolution which is written upon all created things."

In a note Dr. Irving calls attention to the relations, at once of contrast and of similarity, existing between silicon and carbon. Will they ever, as Brown hoped, be found mutually convertible?

Chemists, we think, will feel a deep interest in the study of the work before us from the able and successful manner in which the author applies chemical laws to the elucidation of geological problems.

Watts' Dictionary of Chemistry. Revised and entirely Re-written by M. M. Pattison Muir, M.A., and H. Forster Morley, D.Sc., assisted by Eminent Contributors. In Four Volumes. Vol. II. London and New York: Longmans, Green, and Co.

We are glad to find that the publication of the new edition of Watts's great work is making good progress. The present volume extends from chenocholic acid to indigo, inclusive, and comprises such important subjects as classification, dissociation, earths, elements, chemical equilibrium, equivalency, formulæ, geological chemistry, and indigo.

As a general rule, the information supplied is on a level with the most recent discoveries, in as far as these can be regarded as definitely established. In some cases, indeed, the views taken by the different writers are not absolutely in accordance. Thus, the author of "Earths" speaks decidedly of neodymium and praseodymium as "elements." In the article "Elements," on the other hand, we find these two bodies referred for the present to a provisional class, such as "meta-elements."

If a choice can be made among the longer articles, all of which are of high ability, the article on "Elements" must bear the palm. The author evidently inclines to the belief that the simple bodies of chemistry have been formed from something still simpler, or possibly from one primary form of matter, by some process of evolution not yet understood. The arguments in favour of this new view are summarised clearly and forcibly, but impartially. The writer is of opinion, however, that if "a transmutation of so-called elementary matter should ever be effected in the laboratory, it will be by the very slow development, under conditions of prolonged chemical stress, of change in traces only." In other words, if transmutation is effected, it will not be in some sudden manner, capable of being exhibited on the lecture table, and still less will it admit of industrial execution.

In discussing Prout's law, he concludes that some law approximating to, if not identical with, that proposed by Prout, actually exists.

Under "Cobalt," we find no discussion of its alleged decomposition into two bodies, the true cobalt, and an accompanying impurity, which, as Dr. Krüss alleges, is also found accompanying what has hitherto been regarded as pure nickel.

Germanium and its compounds are very fully and carefully treated; and the same must be said of gallium.

Decipium is regarded as doubtful, and Davyum is mentioned as requiring re-investigation. Didymium is also a subject for doubt: if an element, it is referred to Group V., along with N, P, and eepecially Bi. Concerning its supposed components, neodymium and praseodymium, it is remarked that if salts of the two are mixed in certain proportions the spectrum is the same as that of didymium. This is not quite the case, as the spectrum of didymium contains a residual band not to be found in either that of neodymium or praseodymium.

Two features of the book deserve especial notice, as likely to prove a great convenience to the reader. One is that to several of the more important articles there is appended a carefully compiled bibliography of the subject; the other is a flexible card attached to the binding by ribbon, and capable of serving as a book mark; upon it are printed the many abbreviations, both of the names of journals and transactions cited as authorities, and of the technical terms employed. By these abridgments a great economy of space is effected, and the idea of placing them so as to obviate the frequent references to the beginning of the volume seems to us exceedingly happy, and will be generally appreciated, as will be the work altogether.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—"Cyclops" is in error again. In his last letter (Chem News, lx., p. 245), he suggests, after conceding all my claims as to the *effects* of "Aminol," that by these very effects the "Amines" sludge is rendered useless as a *manure*, because the combined nitrogen which it contains can become available as a plant food only by decomposition or *nitrification*.

The facts are these:—*Putrescible* sludges, unless *speedily* reduced to dryness (which involves expenditure) waste their nitrogen in the process of putrefractive decomposition. The "Amines" sludge, on the contrary, being *non-putrescible*, preserves all of its nitrogen and may be dried slowly and inexpensively by simply spreading it on land. When sufficiently air-dried, its nitrogen becomes available for *nitrification* in the soil, when applied as manure. So much for the value of the sludge as to nitrogen. How about the other plant foods constituting the value of a manure, such as potash, phosphoric acid, and last, but not least,—lime? Is "Cyclops" not aware that lime "is a *direct* plant food; that no crop can grow to perfection without lime, that it favours the formation of nitrate of potash in the soil; that the functions of lime in living plants are connected with the building up of the tissues and the formation of the cell walls, and that its mechanical effect upon coarse sandy, as well as upon fine alluvial soil, and also upon peaty and upon clay lands, is highly benificial and of vast importance?" (See Griffith, on Manures, pp. 232—248).

"Cyclops" is also wrong in assuming that the formation of Aminol *alone* governs the quantity of lime used in the "Amines" process; the degree of clarification required and other considerations play an important part in the determination of the proportions.

"Cyclops" gives it as his opinion that from 45 to 50 grains of lime per gallon are quite impracticable quantities when applied to large flows of sewage; he does not, however, support this opinion by argument. My experiments, per contra, have established not only the entire practicability, but even the true economy of the proportions which I employ.

Allow me to suggest, in conclusion, that your correspondent's criticisms might be better appreciated were he to sign his real name, like—Your Obedient Servant,

Hugo Wollheim.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
November 18, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In reply to Mr. Alf. W. Stokes, can he prove my statements to be wrong? The original Wanklyn method I know, the Somerset House method I know, and the Soxhlet plaster-of-paris method I know; but I have had little or no experience in the Soxhlet areometric process, and much less of the lactocrite.* I therefore regret extremely I cannot comply with Mr. Stokes's request and give him the information he desires. The Schmid process has been under my consideration for some considerable time, but I must confess I have been unable to obtain such concordant results as those obtained by Mr. Stokes. However, I may mention, for Mr. Stokes's benefit, that I have a modification of Schmid's method, giving very satisfactory results, and which I hope to make use of at some future date. Mr. Stokes states:—"It is singular that all these should agree with the calculated results." Why should they not? One would naturally expect them to do so when the particular formula is employed which belongs to that particular process.

I said nothing about "the now generally discarded Wanklyn method," which has long been known not to give accurate results.

Might I now ask Mr. Stokes to give us a series of comparative results obtained from the various processes he has mentioned in his communications to you, and also the formulæ he uses to obtain the calculated results.—I am, &c.,

William Johnstone.

City Central Laboratory,
13, Fish Street Hill, Nov. 17, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Nots.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 18, October 28, 1889.

The Equilibrium of Distribution of Hydrogen between Chlorine and Oxygen.—H. Le Chatelier.—The author gives a formula of equilibrium for a mixture of oxygen, chlorine, water, and hydrochloric acid.

Certain Double Nitrites of Ruthenium and Potassium.—A. Joly and M. Vézes.—The author has obtained two double nitrites, which do not agree in composition with those of an analogous compound obtained by Claus.

Fixation of Nitrogen by Leguminous Plants.—E. Bréal.—Nodosities may be produced on the roots of such plants by pricking them with a needle which has previously been plunged into a nodosity of another plant o

* By Harold Faber the lactocrite is inaccurate when used on skim-milk to the extent of 0·2 per cent.

the same family. The nodosities are full of bacteria, which enable the plant to fix atmospheric nitrogen. An experiment was made with haricots sown in gravel and sand free from nitrogen. The plants were watered with a known quantity of water, containing less than 0·100 grm. of nitrogen. The nitrogen fixed by the plants was 1·4872 grms., and that absorbed by the soil 0·4810, or a total of 1·9682 grms. The cultivation of leguminous plants during the last two years enables the author to conclude, in accordance with Hellriegel, Wilfarth, and Berthelot, that these plants can grow and develop themselves in soils poor in nitrogen if their roots are furnished with nodosities, by means of which they are able to fix atmospheric nitrogen. Hence they are justly called ameliorating crops.

On Ground-Air.—Th. Schlœsing, Jun.—All other things being equal, the proportion of carbonic acid varies considerably at different points. On slopes near the bottom of a valley the air is richer in carbonic acid at the lower points than at the upper. The ground-air must not be supposed to be in a state of rest.

On Sorbite.—C. Vincent and M. Delachanal.—All the fruits of the *Rosaceæ* contain sorbite, along with a sugar capable of fermentation. From pears the authors have obtained 8 grms. of sorbite per kilo., and from cherries grms.

Researches on Crystalline Digitaline.—M. Arnaud.—Crystalline digitaline is a definite chemical species, and there is no reason for designating the pure product as digitoxine. It seems to be the type of a series of analogous bodies, among which must rank tanghinine.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., September, 1889.

Experimental Researches on the Periodic Law.—H. Bohuslav Brauner.—From the *Journal of the Chemical Society*.

Properties of Selenic Anhydride.—Messrs. Cameron and Macallan.—Taken from the Chemical News.

Falsifications of the Vegetable Oils of Commerce.—Paul S. Girard.—A continuation of a valuable memoir, which does not admit of abstraction.

Nitrate of Soda and the Nitrate Country.—Ralph Abercromby.—From *Nature*.

Assay of Palm and Copra Oils.—Calixte Ferrier.—The fatty acids derived from the decomposition of these oils saturate a much larger proportion of base than do the fatty acids from the oils of olive, colza, earth-nut, sesame, linseed, poppy, &c. The fatty acids of palm oil and copra may be split up by crystallisation from alcohol, by pressure, and by fractionated distillation. The following quantities of normal potassa are required for saturating the various fatty acids:—Palm, 21·8 c.c.; copra, 23·6; cotton, 18·4; earth-nut, 17·8; olive, 18·0; sesame, 17·7; tallow, 17·6; lard, 17·4; resin (Bordeaux), 13·2.

Nut Oil.—Th. Bruce Warren,—From the Chemical News.

Gymnemic Acid.—D. Hooper.—From the Chemical News.

Determination of Free Alkali in Soaps.—A. Wilson.—From the Chemical News.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—A mathematical paper, having no direct bearing upon chemistry.

Recognition of Blood.—W. P. Mason.—From the Chemical News.

The Great Chemical Industry at the Exhibition of 1889.—P. Kienlen.—An account of the manufactures of sulphur from different sources, of carbon disulphide, and of sulphurous acid, the sulphites, and the hyposulphites.

On Thiocamf—A New Disinfecting Agent.—Emerson Reynolds.—From the Chemical News.

Industrial Society of Mulhouse.—Session of the Chemical Committee, July 10, 1889.—A new salt of antimony, bearing the name of vomitartarine, and made by Finck, of Stuttgart, was exhibited and handed over for examination to M. Schœelhammer.

R. Bourcart gave a communication on the use of uranium acetate as a mordant for silk and wool.

A sample of tempered mica was submitted to the meeting, and will be examined by M. Camille Schœn.

M. Fehr finds that the diazosulphonic acids obtained by the double decomposition of diazo-chlorides with sodium bisulphite remain unchanged in presence of alkaline phenols as long as the mixtures are kept in the dark, but combine with the formation of oxy-azo- colouring-matters under the influence of the solar rays. Trials made with a certain number of chemical agents (both oxidisers and reducers) to effect combination gave no result.

The Presence of Tin in Certain Sugars, the Means of its Detection, and its Possible Influence upon Public Health.—Dr. Phipson.—From an English source, which is not named.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Lump Camphor.—Can any correspondent tell me of a manufacturer in England of "lump" camphor?—Medicus.

MEETINGS FOR THE WEEK.

Monday, Nov. 25th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 26th.—Royal Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
Wednesday, 27th.—Society of Arts, 8. "Scientific and Technical Instruction in Elementary Schools," by J. Hall Gladstone, Ph.D., F.R.S.
Thursday, 28th.—Institute of Electrical Engineers, 8.
Saturday, 30th.—Royal, 4. (Anniversary).

Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at Robert Rumney's, Ardwick Chemical Works, Manchester

Silicates of Soda and Potash in the state of Soluble Glass, or in CONCENTRATED SOLUTION of first quality, suited for the Manufacture of Soap and other purposes, supplied on best terms by W. Gossage and Sons, Soap Works, Widnes, Lancashire.
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FOR SALE.—The Chemical Gazette.
Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," Chemical News Office, Boy Court, Ludgate Hill London, E.C

TO BE SOLD, the Lancashire Manure Company's Works at Widnes, with Machinery and 4,420 square yards of Freehold Land.—Address, J. Hosking 16, Fenwick Street, Liverpool

THE CHEMICAL NEWS.

VOL. LX. No. 1566.

A NEW PROCESS FOR THE VOLUMETRIC ESTIMATION OF BROMINE IN PRESENCE OF CHLORINE AND IODINE.

By NORMAN McCULLOCH.

IT may not be that the new process to be described will be considered as possessing superior practical features to the best yet devised for the accurate estimation of bromine in presence of chlorine; but if only as projecting a little novelty on the solution of this problem, no apology need preface its publication.

It takes its origin in a new method for volumetrically estimating iodine in presence of chlorine and bromine (CHEM. NEWS, vol. lvii., p. 135), a process which consists in the titration of the hydrochloric acid solution of the iodine or iodide with standard permanganate until the free iodine is converted to the colourless monochloride, a point indicated by means of chloroform.

This procedure is also applicable, although with only approximate accuracy, to the estimation of bromine. The solution to be examined is placed in a glass stoppered bottle, mixed with about one-third of its bulk of strong hydrochloric acid, and a little chloroform added as indicator. The whole is now titrated with permanganate, shaking well after each addition, until the colour of the chloroform ceases to grow paler. The sources of error in the method are due, firstly, to want of sharpness in the end reaction; secondly, the reducing influence of the chloroform on the free bromine and chloride of bromine; and thirdly, formation of a small proportion of manganic chloride, a compound which does not instantaneously react with bromine to the formation of manganous chloride and chloride of bromine.

I use the above method for approximating the amount of bromine to be determined by the more accurate process now to be described, and the facts underlying which are briefly as follows:—

I. When permanganate is added to hydrochloric acid containing a sufficient proportion of manganous chloride, manganic chloride (Mn_2Cl_6) is formed—no chlorine being liberated—*and this compound is unacted upon by hydrocyanic acid.*

II. Bromine and iodine, free or combined with hydrogen, reduce manganic chloride, and are converted to the monochlorides; thus, in the case of hydrobromic acid:—

$$HBr + Mn_2Cl_6 = HCl + BrCl + 2MnCl_2.$$

III. Chlorine, bromine, iodine, and their compounds with each other are reduced by hydrocyanic acid, and as shown in the followlng typical equation:—

$$2Cl + HCN = HCl + CnCl.$$

Taking the facts so far, it follows that when permanganate is added in excess to a hydrobromic and hydriodic acid solution containing the required proportion of manganese chloride, hydrochloric acid, and hydrocyanic acid, chloride, bromide, and iodide of cyanogen are ultimate products of the reaction.

The formation of these compounds may be considered as preceded by that of manganic chloride,—

$$8MnCl_2 + 16HCl + K_2Mn_2O_8 = 5Mn_2Cl_6 + 2KCl + 8H_2O$$

(a reaction in which, I think, oxidation of the manganese precedes its conversion to manganic chloride), this compound then reacting with the bromide and iodide, to the consequent formation of the monochlorides of bromine and iodine, and reduction of these by the hydrocyanic acid—

$$HBr + HI + 4HCN + 2Mn_2Cl_6 = CrBr + CrI + 2CrCl + 4MnCl_2.$$

It will now be understood that, as the amount of manganic chloride reduced is in proportion to that of the bromine or iodine present, the estimation of the non-reduced salt will enable us to calculate the amount of these halogens. This estimation can readily be effected, and by means of the iodine process alluded to in the opening of this article. Excess standard potassium iodide is added to the solution, then a little chloroform, and the whole titrated with standard permanganate until the violet colour of the indicator is discharged. The reaction may be equated thus:—

$$Mn_4Cl_6 + 2HI = 2MnCl_2 + 2I + 2HCl.$$

$$10I + 16KCl + K_2Mn_2O_8 = 10ICl + 2KCl + 2MnCl_2 + 8H_2O.$$

I may also point out that a little of the iodide of cyanogen will take part in the reaction; so—

$$CNI + HI = HCN + 2I,$$

but without, in the nature of the process, having any effect on the ultimate result; and I have shown, in my experiments on the method (and further proved by recent unpublished results), its applicability to the estimation of iodine in presence of hydrocyanic acid.

Hydriodic acid has no action on chloride and bromide of cyanogen, at any rate under the conditions of my process.

I trust that the principle of my method for volumetrically estimating bromine is now clear, and I may proceed to the details of its application.

The required standard solutions of permanganate and potassium iodide are of decinormal and seminormal strength respectively.

The former is prepared by dissolving 31·9 grains potassium permanganate in 10,000 grms. of water; and, as the salt is never quite pure, the solution requires standardisation, which is most accurately and conveniently effected as follows:—

A known weight of from 3 to 5 grains pure dry iodine is dissolved in a little caustic soda Aq contained in glass-stoppered bottle of about 5 ozs. capacity, acidulated with ½ oz. or so of strong hydrochloric acid, the stopper replaced, and bottle and contents cooled. The permanganate is now run in until the solution is nearly decolourised, a little chloroform added, and the violet colour communicated to this by the free iodine liberated, discharged by further but more cautious titration with the permanganate, shaking well after each addition.

The discharge of iodine colour from the chloroform indicates—what already has been equated—conversion of the free iodine to the colourless monochloride by the chlorine liberated in the reaction of the permanganate with the hydrochloric acid.

The iodine equivalent of the permanganate is calculated to bromine by multiplying by the factor 0·6713, and each division (10 grains) equals about 0·04 grain Br considered as the hydracid.

The potassium iodide solution (82·78 grains KI in 10,000 grains H_2O) is also standardised, and with the permanganate by the foregoing process for iodine. Bulk for bulk, it should be equivalent to the permanganate, and likewise delivered from a burette graduated to tenths of a division.

The other reagents requiring note are chloroform, a three per cent solution of hydrocyanic acid, and a strong solution of manganous chloride.

The chloroform—pure or methylated—is treated to dispose of any oxidising or reducing constituent by being well shaken with a few divisions of the permanganate and sufficient hydrochloric acid to decompose this. Enough potassium iodide to liberate free iodine is now added, and the colour so communicated to the chloroform discharged by just the requisite amount of permanganate. Finally, the chloroform is washed free, or nearly free, from acid liquor.

The hydrocyanic acid is simply a potassium cyanide

solution decomposed with excess hydrochloric acid, and titrated with permanganate until it acquires a faintly permanent pink colour, in order to destroy oxidisable impurity. Six hundred grains of KCN (95 per cent) are dissolved in 13½ ozs. of water, transferred to solution bottle, and cooled to as low a temperature as conveniently possible, to which end a frigorific solution consisting of ammonium chloride and potassium nitrate in equal bulks, dissolving in water, may be employed. Two and a half ozs. of hydrochloric acid are diluted with their own volume of water, cooled as foregoing, and added to the cyanide solution—an operation which should be performed in a draught, or well ventilated acid chamber. At this point, any carbonates present in the original cyanide will conduce to loss of HCN, through evolving carbon dioxide; and since these experiments it has occurred to me that it would be advantageous to treat the cyanide solution before acidulation with excess barium chloride and filter off the precipitated carbonate.

The acidified solution is cooled, if warm, to the ordinary temperature of the air, and titrated with permanganate until permanently pink in colour.

The manganous chloride solution consists of a half-pound of the crystallised salt ($MnCl_2+4H_2O$) dissolved in 4 ozs. of warm water and cooled; it contains, per vol., 58 per cent of manganous chloride ($MnCl_2$). The use of a manganous salt for the purpose herein described recalls that in connection with Marguerite's process for estimating iron, to prevent the inimical action of free hydrochloric acid; in both cases the prevention of the liberation of free chlorine is the object desired, and to this effect the manganous salt must bear such a proportion to the free hydrochloric acid as to react with the permanganate before the latter has time to bring about its own ultimate effect in the liberation of free chlorine. A solution containing one-third of its volume of strong hydrochloric acid is amply provided with the salt ($MnCl_2$) in the ratio of three molecules to four of the hydrochloric acid (HCl), and will do with less on lowering its percentage of acid by dilution. From 300 to 500 grains of the manganese solution have been used in my estimations, and an ounce will suffice even in the case of the greatest convenient amount of bromine likely to be determined—3 grains or so; it is impossible to err in the way of using too much, barring the inconvenience of a bulky solution, but too little would mean high results.

We do not find, however, that manganese chloride prevents the liberation of free chlorine in the well-known spontaneous decomposition of manganic chloride. Presumably the unstable chlorine atoms in the contiguous molecules of manganic chloride combine to form free chlorine, and free chlorine is unable to effect direct combination with chloride of manganese; the consequence of this is that manganic chloride is not absolutely stable even at low temperatures. Its rate of decomposition is accelerated by heat and the presence of hydrocyanic acid; but, under the conditions of my process, is sufficiently slow for all practical requirements. For instance, the manganic chloride from the reaction of about 30 divs. permanganate does not undergo appreciable decomposition within half an hour, but in double that time may do so to the extent of about one-tenth of a div., and proportionately more for a longer time.

I used as the standard bromide in my estimations pure sodium bromide, prepared by distilling excess bromine, in presence of potassium bromide, into a pure caustic soda solution, evaporating to dryness, calcining at a low red heat, and preserving in a well stoppered bottle.

The estimations were conducted in a bottle same as described in connection with the standardisation of the permanganate.

The weighed bromide was dissolved in a quantity of water, not exceeding half an ounce in volume, and treated with about an ounce of the manganese solution. The standard permanganate was run in, and in excess of from 10 to 30 divs. of the theoretical requirement. The bottle was then plunged into a frigorific solution—such as already described (and of which a handful of the salts dissolving in a few ounces of water sufficed)—for several minutes to cool its contents to a temperature not exceeding 55° F. Thereafter the bottle was removed and a rotary movement imparted to its contents, and hydrochloric acid slowly added to dissolve the manganic hydroxide; usually about half an ounce of strong HClAq was added, the point being to ensure a sufficiency, or about one third, certainly not less than one-fourth in bulk of the total volume of the solution. Excess of the hydrocyanic acid—30/60 grains—was then added, the bottle re-corked and replaced in cooling solution, and time allowed for the reaction to complete, for which half an hour sufficed when the excess of permanganate was as stated, and ensured from an approximate determination of the bromine by the quick and convenient method already described. The solution was then titrated with standard iodide until it became nearly quite decolourised from the complete decomposition of the manganic chloride, and then slightly re-coloured from liberation of free iodine, indicating excess of the iodide by about half a div. Lastly, the excess iodide was accurately determined by adding a little chloroform and titrating with permanganate in the usual way.

The bromine is calculated simply by taking the difference between the amounts of bromine represented by total permanganate and iodide used.

The results tabulated are the latest obtained. Each div. of the permanganate solution was equivalent to 0·0392 grain Br, considered as the hydracid (HBr), as likewise that of the standard iodide.

Br taken. Grms.	I taken. Grms.	Standard $K_2Mn_2O_8$ used.	Standard KI used.	Br found. Grms.
1·024		35·2	8·8	1·034
0·784		31·2	11·2	0·784
1·032		40·6	14·3	1·031
0·287		11·8	4·6	0·282
1·941		80·4	30·8	1·945
0·287		15·9	8·8	0·278
2·717		80·2	10·9	2·716
0·132		15·4	11·7	0·145
0·271		13·3	8·2	0·278
0·442	0·634	30·2	8·8	0·439
0·450	1·891	50·4	8·9	0·435

It will be seen from the two experiments footing the list in the above Table, that iodine, when present, was, of course, determined as bromine, and so had to be allowed for; consequently where the bromine is in association with iodine the latter must be separately determined by the permanganate-hydrochloric acid method, in order that this deduction be made.

The volumetric process is applicable to the estimation of bromine in presence of all substances with which, so far as my knowledge goes, it is likely to be commercially associated, excepting, of course, oxidising and reducing agents and metals forming bromides insoluble in dilute hydrochloric acid.

To the above results, testifying its accuracy, I couple the assurance of its, comparatively speaking, great convenience.

Laboratory of Clyde Iron Works,
(by Tollcross) Glasgow.

Royal Institution.—The Christmas Lectures (adapted to a Juvenile Auditory) will this year be given by Professor A. W. Rücker, F.R.S., Professor of Physics in the Normal School of Science and Royal School of Mines, on "Electricity." They commence on Saturday, December 28th.

NOTE ON THE

COLORIMETRIC METHODS FOR THE DETERMINATION OF NITRATES IN POTABLE WATERS.

By Dr. SAMUEL RIDEAL,
Lecturer on Chemistry at St. George's Hospital.

HAVING recently had occasion to estimate the amount of nitrates present in some exceptionally pure waters, we have had an opportunity of comparing the results obtained by the well-known colorimetric estimation, based on the formation of ammonium picrate and commonly called the "phenol sulphuric acid" method, with that recently described by S. C. Hooker, in which the intensity of the green colour, produced by the addition of a solution of carbazol to the nitrate solution, is a measure of the amount of nitric acid present. Although the former of these has been known for some years, and our method of performing the operations is not very different from that originally proposed by the author, the following details may be of interest to the readers of the CHEMICAL NEWS:—

The solutions required are (*a*) standard potassium nitrate solution containing 0·7215 grm. of the pure crystallised salt in a litre of water or 1 c.c. = 0·0001 grm. nitrogen; (*b*) phenol sulphuric acid solution prepared by dissolving 15 grms. of pure crystallised phenol in 92·5 c.c. of pure re-distilled sulphuric acid free from nitrates diluted with 7·5 c.c. of water.

In addition to the above solutions, pure strong re-distilled sulphuric acid and dilute ammonia solution are also required.

The process adopted was as follows:—A known volume of the water (100 c.c. or 25 c.c., according to its supposed richness in nitrates) is evaporated to dryness in a porcelain dish. To the dry residue 1 c.c. of the phenol sulphuric acid is added, and then 1 c.c. of pure water and 3 drops of strong sulphuric acid, and the mixture gently warmed. A distinct yellow colour then appears if the water contains any appreciable quantity of nitrates. The contents of the dish are then diluted to about 25 c.c. and ammonia added in slight excess. The solution is poured into a narrow Nessler tube (14" × 1"), the dish washed, and the washings added to the liquid in the tube, and the whole diluted to the 100 c.c. mark. The colour of the solution is roughly judged, and is then imitated by repeating the operation with the standard potassium nitrate solution, the quantity of which may vary from 6 c.c. for bad waters to 0·1 c.c. for a water fairly free from nitrates.

Under the above conditions the method yields very good results, but care must be taken, if the preliminary evaporation is not conducted over a water-bath, not to heat the solid residue obtained, and also after adding the reagent and acid the mixture must only be very gently warmed.

The phenol sulphuric acid solution should be prepared some little time before use, as the fresh solution imparts a faint greenish tinge to the yellow of the ammonium picrate, which may mislead the eye accustomed to the ordinary tints obtained by this process. It was found impossible to estimate the colour by means of solutions of ammonium picrate; but Lovibond's tintometer was not tried.

In the carbazol method the standard potassium nitrate solution and pure sulphuric acid are also required as well as the following special reagents:—

(*a*). Silver sulphate solution containing 4·3945 grms. per litre or one in which 1 c.c. will precipitate 1 part of chlorine per 100,000 from 100 c.c. of water.

(*b*). Aluminium sulphate solution free from chlorides and iron, 5 grms. per litre.

(*c*). Carbazol Solution.—0·6 grm. carbazol is dissolved in glacial acetic acid, and the solution made up to 100 c.c. with the glacial acid. For use, 1 c.c. of this solution is withdrawn by a pipette and mixed with 15 c.c. of pure re-distilled sulphuric acid.

It was also found advisable to prepare, as the author recommends, a series of solutions containing 0·03, 0·05, 0·07, &c., parts of nitrogen per 100,000 from the standard nitrate solution by diluting with water. The process is as follows:—To 100 c.c. of the water, the amount of chlorides in which has first been ascertained, sufficient of the silver sulphate solution is added from a burette to precipitate all the chlorides. To this solution, containing the silver chloride in suspension, 2 c.c. of the aluminium sulphate solution is added, and the whole made up to a convenient bulk, 110 c.c. in the case of waters containing 1 to 6 parts of chlorine per 100,000. The solution is then filtered, and 2 c.c. of this filtrate are then taken for the nitrate estimation, and, of course, the amount found must be calculated from the diluted bulk of the solution. To the 2 c.c. of the filtered water contained in a test-tube, 4 c.c. concentrated sulphuric acid is added, and the mixture well cooled. 1 c.c. of the carbazol solution in sulphuric acid as above described is then added, and a bright green colour appears in a few moments if nitrates are present. The amount of nitrate is roughly gauged from the colour produced, and 2 c.c. of the standard nitrate solution, considered to be equal to it, is placed in a second test-tube, and the operation repeated with it and a fresh 2 c.c. of the water under examination at the same time. If the tints are not similar a fresh comparison must be made, and in every case it is necessary to repeat the operation with a fresh quantity of the water, so that the colours may be developed as nearly as possible simultaneously.

The author states that 0·0006 m.grm. of nitrogen as nitrate may be detected by the carbazol method. The removal of chlorides is necessary for accurate results, but the filtration does not take much time when aluminium sulphate solution is added as described. As the waters under examination were free from iron, we had no opportunity of noticing the effect of the presence of iron on the results. Subjoined is a table showing the amount of nitrates found in five waters of very different character by the two processes.

Nitrogen in Parts per 100,000.

Sample.	Phenol sulphuric acid.	Carbazol.
1	0·025	0·0247
2	0·050	0·045
3	0·200	0·209
4	1·400	1·38
5	1·600	1·65

THE IODINE ABSORPTION OF ESSENTIAL OILS.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

IN the CHEMICAL NEWS (vol. lx., pp. 236 and 245) there appeared two communications—one from Mr. R. A. Cripps, the other from Mr. H. W. Snow—with reference to certain results which I published in the CHEMICAL NEWS (vol. lx., p. 175) in connection with the iodine absorption of essential oils. I should like to make a few observations in reply to the above.

Mr. Snow had already been kind enough to send me (through the courtesy of the Editor of the CHEMICAL NEWS) cuttings from *The New Idea* containing the results of the investigation mentioned in his letter, for which I beg to thank him. I regret having overlooked the work previously done by Messrs. Davies and Snow in this direction, when searching the literature of the subject, as I was most anxious to compare my results with those of other observers. I quite endorse Mr. Snow's statement that determination of the iodine absorption of essential oils is likely to prove extremely useful as an indication of their purity or otherwise. The test must, of

course, be performed under certain specified conditions, or the results obtained will be altogether misleading, but the same may be said of many other well-known analytical processes.

When I was engaged upon the investigation in question, it seemed to me preferable to allow the chloroformic solution of the various essential oils to remain in contact with Hübl's reagent for four hours, that being, I believe, the period of digestion adopted by most analysts in the case of fixed oils and fats. I was aware of the fact that the iodine absorption of many essential oils is incomplete in four hours, but the same remark frequently applies even when the digestion is permitted to go on for the length of time recommended by Mr. Davies, viz., eighteen hours. This point is well brought out in some of the results quoted by Mr. Snow in his original paper. As a case in point, I may also call attention to a sample of oil of peppermint which I examined last week. I found the iodine absorption, under varying conditions, to be as follows :—

Hours.	Per cent.
4	46
6	46
24	67
48	102

If necessary, I could give numerous instances where a distinct advantage is gained by allowing the iodine absorption to proceed for only four hours, instead of eighteen hours or longer. Take, for example, an oil of peppermint adulterated with turpentine. The iodine absorption of genuine oil of peppermint being rather low in four hours, while, on the other hand, turpentine (which has a very high iodine absorbing power) takes up almost its full amount of iodine in that time, it is obvious that if the reaction were allowed to proceed for, say, eighteen hours, the detection of a small proportion of turpentine would be rendered more difficult, owing to the fact that any increase in the iodine absorption would be mainly due to the oil of peppermint, and only slightly due to the adulterant.

In some cases, however, it would probably be useful to determine the iodine absorption in eighteen hours as well as in four hours.

When we remember the widely different conditions under which Mr. Davies and I worked, the fairly close agreement between many of our results is, I think, remarkable. In the case of the oils of bergamot, caraway, and lemon, our respective figures were as follows :—

	Davies.	Williams.
Bergamot	276·1	247·9, 283·7
Caraway	254·9	258·3, *263·2
Lemon	†344·5	320·16, 322·96

There can, I think, be no reasonable doubt that had my determinations been permitted to stand for eighteen hours there would have been even greater concordance between all our figures. I shall take the first convenient opportunity of repeating the iodine absorption during eighteen hours of all the essential oils which I have at hand, in order to satisfy myself on this point.

I ought, perhaps, to call attention to the fact that as the iodine absorption of most essential oils is very high, compared with that of the fixed oils, it is only to be expected that somewhat greater discrepancies will occur between different samples of the former than between those of the latter. Nevertheless, I feel confident that determination of the iodine absorption will frequently be found useful in the examination of essential oils for the numerous adulterants to which they are peculiarly liable.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
November 19, 1889.

* Wrongly quoted by Mr. Cripps as 463·2
† Average of seven samples.

A SOURCE OF ERROR IN SEPARATING SMALL QUANTITIES OF MANGANESE FROM A LARGE QUANTITY OF LIME BY AMMONIUM SULPHIDE.

By L. BLUM.

In precipitating manganese by ammonium sulphide, R. Fresenius proposes to allow in all cases the lapse of at least twenty-four hours, but, in very dilute solutions, forty-eight hours before filtering.

In the analysis of Luxemburg blast-furnace slags, where small quantities of manganese have to be determined in presence of much lime, and in consequence large weights have to be taken for analysis, it has occurred to the writer that in allowing the solution, reduced to a small volume, to stand for some time, there was separated out along with the manganese sulphide another crystalline compound, which rendered the results too high.

The compound was obtained pure by allowing a concentrated solution of calcium chloride mixed with yellow ammonium sulphide to stand for some time, with access of air. The compound separated out in crystals, which adhered firmly to the glass. A qualitative examination showed that it was calcium hyposulphite.

In those cases, therefore, where, in consequence of the co-existence of a little manganese and much lime, a strong concentration of the liquid is requisite, it seems not advisable to allow the precipitate to settle too long. It is then better to proceed according to the process given by Finkener, who filters off the precipitate of manganese sulphide at once after a good ebullition and the addition of a further dose of ammonium sulphide. On proceeding in this manner a deposit of calcium hyposulphite has never been observed.—*Zeitschrift f. Analyt. Chemie*, Part iv., p. 454.

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and LEE K. FRANKEL.

I. *Separation of Cadmium from Copper.*

The results obtained in the electrolysis of cyanide solutions of mercury and copper, as well as the knowledge gained from our experiments in separating cadmium from zinc, induced us to try whether it would be possible to effect the evaporation of cadmium from copper in cyanide solution. The only electrolytic method proposed for the separation of these metals is that recommended by Smith (*Am. Chem. Journal*, ii., 42), in which solutions con-

Cadmium present. Grm.	Cu present. Per cent.	Cadmium found.
	I.	
0·2426	50	0·2420
	II.	
0·2318	50	0·2331
	50	0·2309
	50	0·2315
	III.	
0·1024	100	0·1028
	100	0·1019
	100	0·1020
	100	0·1032
	100	0·1033
	100	0·1034
	100	0·1014
	IV.	
0·2046	100	0·2034

taining a definite amount of free nitric acid were employed. We experienced no difficulty in making a complete separation, after ascertaining the proper current strength. The conditions most favourable for the separation were essentially the same as those recorded in our former papers, viz.: a dilution of 200 c.c.; 5·5 grms. of potassium cyanide in each experiment, and a current generating 0·28 c.c. oxy-hydrogen gas per minute. Time, sixteen to twenty hours. The results obtained were as in Table.

Copper was not found in any of the deposited cadmium, nor did we discover any of the latter metal in the filtrate containing the copper. The cadmium deposit invariably showed the grey colour characteristic of it.

II. *Action of the Current upon Metallic Sulphocyanides.*

It is well known that in the electrolysis of the sulphate or nitrate of manganese, the oxide of this metal separates upon the positive pole. We have found that if an excess of potassium sulphocyanide be present no such deposition occurs, but, on the contrary, the metal itself will separate as a greyish white, compact deposit upon the negative pole or the vessel attached to it. The addition of a sulphocyanide to the manganese solution undergoing electrolysis, after the oxide has already separated, will cause the solution of the latter. The current necessary for the deposition of metallic manganese, under the conditions mentioned above, should be feeble. The metallic deposit is inclined to rapidly oxidise, and whether manganese can be successfully determined in a quantitative way after this manner will depend very much upon whether we can prevent its oxidation during the drying process.

Nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current.—*Journal of the Franklin Institute*, August, 1889.

SOME CONSIDERATIONS IN REGARD TO THE FORMATION OF COAL AND CARBONACEOUS MINERALS.

By W. A. DIXON, F.I.C., F.C.S,
Lecturer on Chemistry, Sydney Technical College.

In most chemical manuals the production of coal and similar carbonaceous minerals from cellulose is assumed, and equations are given, showing its transformation into coal of different varieties by the elimination of oxygen and hydrogen as water, carbon and oxygen as carbon dioxide, and carbon and hydrogen as methane. These are known to be evolved during the decomposition of vegetable matter, and are assumed to be given off by cellulose, and as this has a high molecular weight, and as any acquired number of molecules may be used, the equations look very pretty. One can subtract any acquired number of molecules of CO_2H_2O and CH_4 from $C_6H_{10}O_5$, or a multiple of it, and obtain a residue corresponding to anything, from free carbon to cellulose itself. These views are again set forth in one of the latest chemical works bearing on the subject, viz., "Wanklyn's Gas Engineers' Chemical Manual." In connection with this I would point out that in most coals the woody fibre, which contains the greater portion of the cellulose in modern plants, is represented by almost pure carbon, forming the so-called "mother-of-coal," or mineral charcoal. As cellulose was so converted, it is an untenable position that other portions of the *same* substance should, under the *same* conditions, be converted into bituminous matter.

On the other hand, mineralogists and geologists generally lay great stress on the conditions under which the deposit of coal was formed, and refer particular varieties to different horizons as a reason for their different composition and properties. This can be made to agree with the chemical hypothesis mentioned, as it may be said that different quantities of the products would be formed under varying conditions.

There are others who acknowledge that there are at least three conditions which modify the composition of the mineral. Thus, Percy recognises the fact that difference in the composition of vegetable matter due to resinous bodies, &c., may, by increasing resistance to decomposition, tend to preserve vegetable structure ("Fuel," p. 270). Dana says "Coals were once beds of vegetation, analogous in most respects to the peat beds of modern times" ("Mineralogy," p. 758), and on the succeeding page, "between excluded air and imperfectly excluded, and of pressure from heavy superincumbent earthy beds and little or no pressure lie the conditions which attended the origin of the various kinds of coal, and determined, in *connection with the nature of the vegetation itself*, their transformation in progress." From various observations the writer has come to the conclusion that the words put in italics by himself are of more importance than is usually assumed, and that this idea is probably the most important of all. This condition is placed first in a sentence in Ronalds and Richardson's "Knapp's Technology" (i., p. 765), where it says:—"The varieties of coal may depend on the nature of the plants that composed it, the varied circumstances attending their deposit, or the varied conditions under which the beds have subsequently been placed."

My thoughts were first directed to the probable comparatively great importance of the original composition of the plants through examining a number of brown coals from New Zealand, Victoria, Western Australia, and New South Wales, and which I found could be divided into four classes.

1st. Those containing fossil resin (retinite) distributed through them in grains from the size of pin-heads to that of marbles, and amounting sometimes to 20 or 25 per cent of the mass.
2nd. Those containing iron pyrites but no retinite.
3rd. Those containing neither retinite nor pyrites, but having much sulphur in organic combination.
4th. Those without retinite, pyrites, or much sulphur.

Subjected to distillation, the first and last evolved but little sulphuretted hydrogen, the second evolved much of this gas under the conditions of high temperature, the third both at high and low temperature.

If we consider these varieties of imperfect coal it appears probable that, had they been subjected to conditions such as would convert them into coal, the results would be very different for each, although the conditions were the same. The first is evidently produced from highly resinous vegetation, and would probably yield bituminous coal, and the resin gives an aromatic odoured distillate on quickly heating, but the amount of resin available was too small to go into the matter of the products. The second, from non-resinous vegetation, the pyrites being formed by infiltration, would yield a coal like the stinking coal of Lancashire or the brassy coal of some of the Scotch mines. The third it seems probable was produced from vegetation containing much sulphur, such as we find in our modern Cruciferæ, and to this I know of no corresponding true coals. The fourth would correspond to the splint, cherry, and other less bituminous coals.

Again, the deposit of kerosene shale or torbanite at Joadja Creek consists of three distinct layers, separated by almost imperceptible partings, and yet everywhere perfectly distinct. The seam is composed of, first, a layer of splint coal containing a rather large proportion of ash, second, a layer of shale, covered, third, by a layer of bituminous coal of fair quality. In this case it appears that the three layers were deposited in orderly succession, and that all must have been subjected to the same conditions since deposition, and yet the ultimate products are entirely different. It may be observed, in passing, that these

deposits of torbanite, both in New South Wales and Scotland, where one only has been found, seem to have been originally laid down in irregularly lenticular depressions, and observation has indicated that they have never been subjected to excessive pressure, as wherever the "cover" exceeds two or three hundred feet the torbanite is found changed into a carbonaceous slaty mass. It is evident that the differences in the three layers in this seam cannot be ascribed to any other causes than an originally radical difference in the vegetation forming them. Torbanite, Boghead, or kerosene shale, has been legally classed as coal, and it is usually classed with cannels although it is very different. Thus Wanklyn (*loc. cit.*) says—"The following is an analysis of one of the richest cannels, viz., Boghead" (the original torbanite of Scotland). "The large proportion of mineral matter (21 to 22 per cent) will not escape notice; and it will be perceived that Boghead consists of mineral matter saturated with a hydrocarbon containing a larger proportion of hydrogen than there is in benzine, C_6H_6." At Joadja Creek the mineral matter falls as low as six per cent, and it is difficult, I should say impossible, to think of six parts of mineral matter "saturated" with ninety-four parts of hydrocarbon, whilst the overlying coal and sandstone and the underlying coal and sandstone are absolutely free from it.

The old alchemists used to subject everything organic to distinctive distillation, and divide it into water, phlegm, and caput mortuum, and perhaps some information may be gleamed from this industry as now carried out on a large scale. This information is, however, not very direct, owing to the effect of varying temperatures in process, so that the subject is divided into two, namely, high temperature distillation, *i.e.*, gas-making, and low temperature, *i.e.*, oil-making. In the first the liquid and solid hydrocarbons obtained are mostly composed of the aromatic series, whilst those of the latter belong to the fatty series. The gaseous products may be disregarded in both cases, as they are similar, being hydrogen, methane, and some of the lower olefines, and mixed, in the case of high temperature work, with the vapours of aromatic hydrocarbons held in gaseous solution.

In all high temperature work more gas is produced than in low, and carbon is deposited whilst aromatic hydrocarbons are formed, as benzol from polymerisation of acetylene below a red heat, and its conversion by elimination of hydrogen into naphthalene at a red heat, whatever the source of the original hydrocarbon. If, however, we look at what is done commercially with various coals and shales, we shall find that they are not used indiscriminately, but some for one purpose, some for another, according to the value of the products. The statements sometimes found in books are often rather confusing; thus, Knapp says:—"When submitted to destructive distillation all varieties of coal yield the same solid, liquid, and gaseous products, consisting of coke, tar, ammoniacal liquor, benzol, naphtha, naphthaline, paraffin, paraffin oil, and illuminating gas, the proportions of which vary with the quality of the coal and the temperature employed" (Ronalds and Richardson's "Knapp's Technology," vol. i., p. 273). Later writers recognise some difference; thus, Mills says:—"Cannel tars are poorer in aromatic compounds than are bituminous tars" ("Manualette of Destructive Distillation"), and Lunge:—"We may say generally that the tars from peat, brown coal, and bituminous shale consist principally of hydrocarbons of the 'fatty series,' wood-tar of phenols and their derivatives, coal-tar of aromatic hydrocarbons" ("Distillation of Coal-Tar," p. 3). Again:—"Brown coal-tar, as well as that obtained from peat and bituminous shale (and ormerly from the Torbane Hill mineral) is manufactured for its own sake as a principal product, and forms the basis of the West European manufacture of mineral oils and paraffin. The other products of the destructive distillation of such more recent fossils possess very little or no value, except in the case of some very dense coal-like brown coals, which furnish good coke and good gas, but no mineral oil."

These quotations show the general drift of opinion amongst those intimately connected with the subject of distillation, as I have also been more or less for thirty years. There is a radical difference in the substances submitted to retorting, and although the fatty hydrocarbons are more or less converted into gas and aromatic hydrocarbons by a high temperature, the transformation is always incomplete, and I believe that the difference in products arises chiefly from the original differences of the vegetation of which the coal or shale was formed. Of the various mineral fuels, some, as anthracite and splint and cherry coals, are never distilled, the products being of no value. Cokeing coals (in contradistinction to gas-coals which are used for making both gas and coke) are distilled for the sake of the coke, and a few years since it was anticipated that great results would be obtained by the use of Simon Carvés and other improved ovens by which the tar could be collected, but valuable aromatic hydrocarbons were present in such small proportion that the anticipations were not realised. Bituminous gas-coal yields tar rich in benzine, anthracene, and other valuable aromatic hydrocarbons, and practically none of the fatty series, and tar distillers object to the use of shale along with it, as they introduce these.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

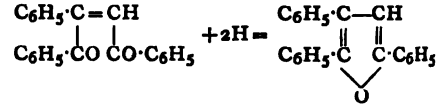
Ordinary Meeting, November 7th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

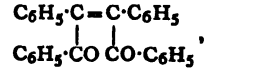
(Concluded fom p. 255).

92. "*αβ-Dibenzoylstyrolene and the Constitution of Zinin's Lepiden Derivatives.*" By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

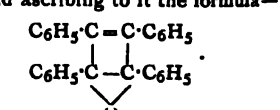
In a preliminary note (*Ber.*, xxi., 2933) the authors showed that by the action of iodhydric acid on αβ-dibenzoylstyrolene (anhydracetophenonebenzyl) triphenylfurfuran was formed:—



An attempt to prepare the corresponding dibenzoylstilbene,—



in order to convert it by the action of iodhydric acid into tetraphenylfurfuran, failed; but the authors pointed out (*Ber.*, xxi., p. 2934, footnote) that possibly Zinin's lepiden, $C_{28}H_{20}O$ (m. p. 175°), was the desired tetraphenylfurfuran. In making this suggestion it had escaped their notice that a similar idea had been put forward by Dorn as early as 1870 (*Annalen*, cliii., 358), Dorn calling lepiden "oxyphenyltetrol," and ascribing to it the formula—



Magnanini and Angeli (*Ber.*, xxii., 853) have since found that Zinin's hydro-oxylepiden is identical with Knoevenagel's bidesyl,—

$$C_6H_5\cdot CH—CH\cdot C_6H_5$$
$$C_6H_5\cdot CO \quad CO\cdot C_6H_5 \quad ;$$

and by the dehydrating action of chlorhydric acid they have converted bidesyl into tetraphenylfurfuran identical with lepiden. They regard Zinin's oxylepiden, $C_{28}H_{20}O_2$, as having the formula of the before-mentioned dibenzoylstilbene. This view would make oxylepiden a strict analogue of dibenzoylstyrolene: as dibenzoylstilbene it is phenyldibenzoylstyrolene.

The authors have been engaged for some time in studying the interactions of dibenzoylstyrolene, and find, in support of the foregoing view, that there is an almost perfect parallelism in behaviour between it and oxylepiden. The various compounds obtained by them stand to the corresponding compounds of the lepiden series in the relation of triphenyl-derivatives to tetraphenyl-derivatives, a relation which is exhibited, in the first place, in the case of dibenzoylstyrolene and oxylepiden themselves. It is necessary to point out, however, that of the three "oxylepidens" prepared by Zinin, the analogue of dibenzoylstyrolene is "acicular oxylepiden" (m. p. 220°).

By heating "acicular oxylepiden" with iodhydric acid, Berlin (*Annalen*, cliii., 131) converted it into lepiden (tetraphenylfurfuran). As already mentioned, the authors have shown that when subjected to the same treatment dibenzoylstyrolene yields triphenylfurfuran.

By heating "acicular oxylepiden" Zinin obtained two isomeric "oxylepidens:" as chief product "tabular oxylepiden" (m. p. 136°), and in small quantity "octahedral oxylepiden" (m. p. 232°). In like manner, by heating dibenzoylstyrolene, the authors have converted it into two isomerides: a compound formed in large quantity, crystallising from alcohol in long, lustrous needles, melting at 117—118°, corresponding with "tabular oxylepiden;" and a compound formed only in small quantity, crystallising from alcohol, in which it is very sparingly soluble, in slender white needles, melting at 197—198°, corresponding with "octahedral oxylepiden." They regard the compound melting at 117—118° as *triphenylcrotolactone*, and "tabular oxylepiden" as *tetraphenylcrotolactone*—

$$(C_6H_5)_2C—CH$$
$$CO\ C\cdot C_6H_5$$
$$O$$

Compound melting at 117—118°.

$$(C_6H_5)_2C—C\cdot C_6H_5$$
$$CO\ C\cdot C_6H_5$$
$$O$$

"Tabular oxylepiden."

On oxidation with excess of chromic anhydride, triphenylcrotolactone yields benzophenone and benzoic acid. Zinin does not appear to have oxidised "tabular oxylepiden," but he obtained benzophenone from isolepiden, which is formed from "tabular oxylepiden" by distillation.

Caustic potash in alcoholic solution converts triphenylcrotolactone into a salt of *α-diphenyl-β-benzoylpropionic acid*. Zinin has shown that "tabular oxylepiden" yields oxylepidenic acid, $C_{28}H_{22}O_3$, when similarly treated. The following formulæ express the authors' views as to the constitution of these two acids:—

$$(C_6H_5)_2C———CH_2$$
$$COOH \quad CO\cdot C_6H_5$$

α-Diphenyl-β-benzoylpropionic acid (m. p. 182—183°).

$$(C_6H_5)_2C———CH\cdot C_6H_5$$
$$COOH \quad CO\cdot C_6H_5$$

Oxylepidenic acid.

Diphenylbenzoylpropionic acid displays the behaviour of lævulic acid and other γ-ketonic acids. Thus it interacts with phenylhydrazine with elimination of *two* mols. of water, yielding the compound $C_{28}H_{22}N_2O$ (m. p. 185°). In a similar manner hydroxylamine converts it into the compound $C_{22}H_{17}NO_2$, melting at 150—152°. Nascent hydrogen reduces it to a γ-hydroxy-acid, which is very unstable, and when liberated from its salts speedily parts with water, yielding a lactone—

$$(C_6H_5)_2C———CH_2$$
$$COOH \quad CH(OH)\cdot C_6H_5$$

Triphenyl-γ-hydroxybutyric acid.

$$(C_6H_5)_2C—CH_2$$
$$CO\ CH\cdot C_6H_5 \quad +H_2O.$$
$$O$$

Triphenylbutyrolactone (m. p. 153°).

This lactone may also be obtained directly from triphenylcrotolactone by boiling it with iodhydric acid.

When heated above its melting-point, diphenylbenzoylpropionic acid is re-converted with loss of water into triphenylcrotolactone, a process which corresponds with the formation of the anhydrides of lævulic acid observed by Wolff (*Annalen*, ccxxix., 249). Zinin has shown that oxylepidenic acid can be re-converted by the dehydrating action of heat into "tabular oxylepiden."

Zinin's "octahedral oxylepiden" and the corresponding compound melting at 197—198°, obtained from dibenzoylstyrolene, are difficult to prepare in quantity, and have not yet been fully examined; but the authors incline to the view that these compounds are stereometric isomerides of "acicular oxylepiden" and *αβ*-dibenzoylstyrolene respectively, and would classify them as follows:—

Maleoid Form.	*Fumaroid Form.*
"Acicular oxylepiden."	"Octahedral oxylepiden."
αβ-Dibenzoylstyrolene (m. p. 129°).	Iso-*αβ*-dibenzoylstyrolene (m. p. 197—198°).

By distilling oxylepiden Zinin obtained from it a compound which he called *isolepiden*, assigning to it the formula $C_{28}H_{20}O$, whilst from the mother-liquors from this substance he obtained, by the action of potash, an acid of the formula $C_{28}H_{22}O_3$, to which he gave the name *isoxylepidenic acid*. The authors, therefore, following this analogy, distilled dibenzoylstyrolene, expecting to obtain from it isomerides of triphenylfurfuran and diphenylbenzoylpropionic acid respectively, but found that dibenzoylstyrolene was converted, with evolution of carbon monoxide, into a compound of the formula—

$$C_{21}H_{16}O = C_{22}H_{16}O_2 - CO,$$

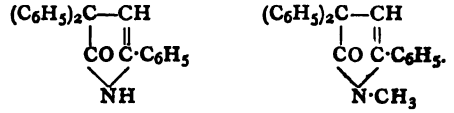
which formed lustrous yellow crystals melting at 92—93°; whilst by the action of potash on the mother-liquors from this compound only ordinary diphenylbenzoylpropionic acid was obtained. As these results were in contradiction to the strict analogy elsewhere observable in the two sets of compounds, they repeated Zinin's experiment on the distillation of oxylepiden, and found that the so-called isolepiden is formed, not by a process of deoxidation, as represented by Zinin, but with elimination of carbon monoxide, $C_{28}H_{20}O_2 = C_{27}H_{20}O + CO$, and is therefore not an isomeride of lepiden at all. The formulæ of the various hydro-"isolepidens" and oxy-"isolepidens" described by Zinin must also, therefore, be correspondingly modified.

From the mother-liquors from the compound $C_{27}H_{20}O$ the authors have obtained the so-called "isoxylepidenic acid," which proves, however, to be not isomeric, as stated by Zinin, but identical with oxylepidenic acid. The "acicular oxylepiden" is converted, during the heating, into "tabular oxylepiden," the greater part of which parts with carbonic oxide, forming "isolepiden," but a small portion distils unchanged and is hydrolysed in the subsequent treatment with alkali, yielding oxylepidenic acid. The analogy is, therefore, preserved also in this case.

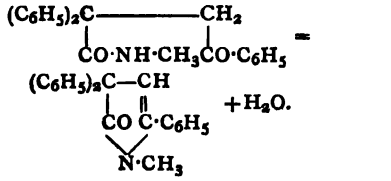
The remaining interactions of dibenzoylstyrolene described in this note have not yet been studied in the lepiden series.

By acting on dibenzoylstyrolene with ammonia the authors obtained (*Ber.*, xxi., 2936) two compounds of the formula $C_{22}H_{17}NO$: one melting at 180°, formed by

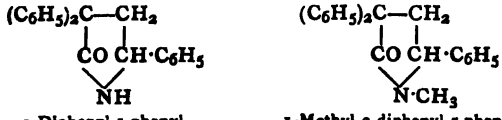
mixing a warm solution of dibenzoylstyrolene with alcoholic ammonia: the second, melting at 221°, formed from the first by long boiling of its solutions, or by heating it alone. They now find that the various primary paraffinoid amines yield similar compounds. As yet only the compound formed with methylamine has been more fully investigated. This compound, which has the formula $C_{22}H_{16}(CH_3)NO$ and melts at 138—139°, and the ammonia compound $C_{22}H_{17}NO$, melting at 221°, can also be very readily obtained by the action of methylamine and ammonia respectively on triphenylcrotolactone. The ammonia compound stands to the methylamine compound in the relation expressed by the following formulæ:—



Adopting a nomenclature based on that employed by Tafel (*Ber.*, xxii., 1861), these compounds would be called *3-diphenyl-5-phenylpyrrholone* and *1-methyl-3-diphenyl-5-phenylpyrrholone*; "pyrrholone" being equivalent to "ketopyrrholine," using "pyrrholine" in the generally accepted sense of "dihydropyrrhole." The latter compound may be obtained from triphenylcrotolactone and methylamine in two stages: in the first, the methylamine of diphenylbenzoylpropionic acid is formed; this, on heating, parts with water, yielding the compound $C_{22}H_{16}(CH_3)NO$—



On reduction with sodium and boiling amyl alcohol, these pyrrholones yield the corresponding dihydro-compounds or *pyrrholidones* — derivatives of tetrahydropyrrhole—

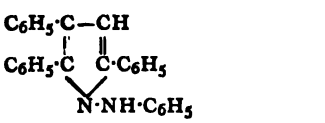


3-Diphenyl-5-phenylpyrrholidone (m. p. 201°).

1-Methyl-3-diphenyl-5-phenylpyrrholidone (m. p. 153·5°).

The pyrrholones in question also yield characteristic oxidation products and bromine-derivatives, which are still under investigation, as are also some remarkable cases of isomerism which the authors have discovered among the compounds formed by the action of alkylamines on dibenzoylstyrolene.

By the action of phenylhydrazine on dibenzoylstyrolene, Japp and Huntly obtained (*Trans.*, 1888, 184) a compound of the formula $C_{28}H_{22}N_2$. The authors regard this as most probably an anilidotriphenylpyrrhole, of the constitution—

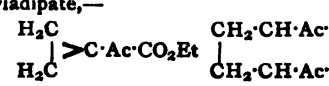


(*cf.* also Knorr, *Annalen*, ccxxxvi., 295). From the products of the same reaction they have isolated two further compounds; a substance, $C_{28}H_{22}N_2O$, melting at 173—174°, which is apparently a monohydrazone of dibenzoylstyrolene; and a second compound, $C_{21}H_{16}N_2$, melting at 206°, formed by the action of the phenylhydrazine with elimination of a benzoyl-group from dibenzoylstyrolene; this appears to be a *triphenylpyrazole*, isomeric with Knorr and Laubmann's 1-3-5-triphenylpyrazole.

With hydroxylamine hydrochloride, dibenzoylstyrolene yields a compound, $C_{15}H_{11}NO$, melting at 73—75°. Like the foregoing phenylhydrazine derivative, with which it corresponds, it is formed with elimination of a benzoyl-group.

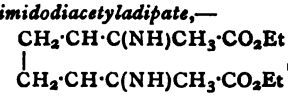
93. "*Ethylic αα₁-diacetyladipate.*" By W. H. Perkin, Jun., Ph.D.

Ethylene bromide and ethylic sodacetoacetate interact readily when heated together in alcoholic solution, forming ethylic acetyltrimethylenecarboxylate and ethylic $\alpha\alpha_1$-diacetyladipate,—

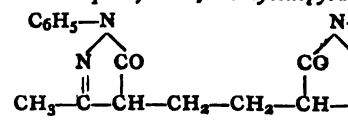


These two substances may be readily separated by distillation in steam, the former passing over with the steam; the diacetyladipate may be extracted from the residue by ether, and is best purified by conversion into the crystalline diimido-compound, which is then hydrolysed by chlorhydric acid. Ethylic diacetyladipate is a thick colourless oil, which gives with ferric chloride a fine violet colouration. On the addition of sodium ethylate to an ethereal solution, a yellowish white precipitate of its disodium derivative is produced, which is readily re-converted by acids into ethylic diacetyladipate.

Ethylic diimidodiacetyladipate,—

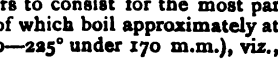


separates from the solution of the ethereal salt in alcoholic ammonia in beautiful colourless plates, which melt at 170°. It readily dissolves in cold dilute acids, but on warming, decomposition into ethylic diacetyladipate and ammonia readily takes place. The corresponding *ethylic diphenylhydrazinediacetyladipate* is formed when ethylic diacetyladipate is warmed with excess of phenylhydrazine. It crystallises from alcohol in light yellow plates, which, when heated above their melting point (145°) are converted into *bis-phenylmethylmethylenepyrazolone*,—

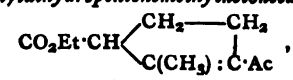


This substance crystallises from acetic acid in small prismatic needles, which do not melt at 250°. It is difficultly soluble in most of the ordinary solvents, but readily soluble in acids and alkalies.

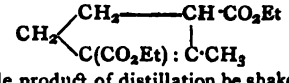
When subjected to distillation under reduced pressure ethylic diacetyladipate yields a yellowish oily distillate, which appears to consist for the most part of three substances, all of which boil approximately at the same temperature (210—225° under 170 m.m.), viz., *ethylic acetyladipate*,—



ethylic methyldihydropentenemethylketonecarboxylate,—



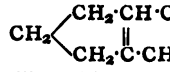
and *ethylic methyldihydropentenedicarboxylate*,—



If the crude product of distillation be shaken with dilute aqueous potash, the ethylic acetyladipate dissolves, forming an acid ethereal salt, which, on distillation, is decomposed into carbon dioxide and ethylic ω-acetylvalerianate, a colourless oil boiling at 200—205° (150 m.m.). *ω-Acetovalerianic acid*, which is readily obtained

from the ethereal salt by hydrolysis, forms a crystalline mass which melts at 40—42°, and distils at 250—253° (280 m.m.) with slight decomposition.

The residual oily product of distillation of ethylic diacetyladipate, which is insoluble in potassium hydrate, yields on hydrolysis two principal products. One of these is a neutral substance, $C_8H_{12}O$, which boils constantly at 191°, and smells strongly of camphor. From its reactions this substance appears to be methyldihydropentenemethylketone,—



It combines readily with hydroxylamine, forming a beautifully crystalline hydroxime, $C_8H_{13}NO$, which melts at 86°; when heated to 100° with Beckmann's reagent (acetic acid, acetic anhydride, and hydrogen chloride) this compound is converted into an isomeric oily substance of pronounced basic properties, which boils at 164—165° and readily dissolves in water, forming a strongly alkaline solution. The platinochloride—

$$(C_8H_{13}NO)H_2PtCl_6$$

crystallises from water in magnificent red prisms.

The second product of hydrolysis, methyldihydropentenedicarboxylic acid, crystallises from water in colourless plates which melt at 188°.

Concentrated sulphuric acid converts ethylic diacetyladipate into a substance of the formula $C_{12}H_{18}O_4$, which appears to be ethylic methyldihydropentene.

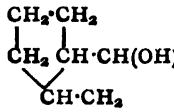
94. "(1·2) *Methylethylpentamethylene.*" By T. Rhymer Marshall, D.Sc., and W. H. Perkin, jun., Ph.D.

Ethylic $\alpha\alpha_1$-diacetyladipate when carefully hydrolysed by alcoholic potash yields α-ω-diacetylbutane,—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

This substance is a white crystalline solid, which melts at 43—44°: it is converted by dehydrating agents, or by boiling with alcoholic potash, into the methyldehydropentenemethylketone described in the previous abstract.

Methylpentamethylenemethylcarbinol,—

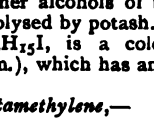


is obtained by reducing methyldihydropentenemethylketone with sodium in moist ethereal solution. It forms a colourless oil boiling at 181°, smelling strongly of menthol.

The *acetate*, $C_8H_{15}OC_2H_3O$, is readily prepared by boiling the alcohol with acetic anhydride. It boils at 133—135° (90 m.m.), has a smell resembling that of the acetate of the higher alcohols of the fatty series, and is very readily hydrolysed by potash.

The *iodide*, $C_8H_{15}I$, is a colourless oil, boiling at 155—160° (90 m.m.), which has an odour resembling that of amyliodide.

Methylethylpentamethylene,—



is produced when the iodide is heated with iodhydric acid and amorphous phosphorus in sealed tubes at 234—240° for eight hours. It is a limpid liquid boiling at 124°, and smelling very like light petroleum. By the reduction of methyldihydropentenemethylketone with sodium in moist ether, a considerable quantity of a secondary product, $C_{16}H_{30}O_2$, is formed, which is a very thick oil boiling at 250—255° (50 m.m.). If sodium amalgam be used as a reducing agent, two substances of complicated composition are formed, *i.e.*, $C_{16}H_{22}O$ (b. p. 220°, 25 m.m. pressure) and $C_{16}H_{24}O_2$ (b. p. 250—260°, 25 m.m. pressure).

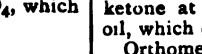
95. "*Action of Dehydrating Agents on α-ω-Diacetylpentane. Formation of Methylethylhexamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

α-ω-Diacetylpentane, under the influence of dehydrating agents, loses one molecule of water and is converted into a compound of the formula $C_9H_{14}O$; although the constitution of this substance has not yet been proved beyond doubt, its formation and its properties seem to show that it has the constitution of an orthomethyltetrahydrobenzene methylketone (orthomethyacetyltetrahydrobenzene,—

This compound is best prepared by dissolving diacetylpentane in concentrated sulphuric acid. It is a colourless mobile oil, boiling at 205—206°, and smelling strongly of peppermint; it is insoluble in water, but is miscible with alcohol, ether, &c., in all proportions. It is not decomposed when heated with water at 150°, or when treated with 80 per cent sulphuric acid at the ordinary temperature; it does not combine with mercuric chloride.

The *hydroxime*, $C_6H_8Me{\cdot}CMe{:}NOH$, prepared by treating the ketone with hydroxylamine chlorhydride and excess of potash in alcoholic solution, is a thick, slightly yellow oil, sparingly soluble in hot water, readily in potash and concentrated hydrochloric acid. The *hydrazone*, $C_6H_8Me{\cdot}CMe{:}N_2Ph$, obtained by heating the ketone at 100° with phenylhydrazine, is a thick yellow oil, which decomposes gradually on exposure to the air.

Orthomethylhexamethylenemethylcarbinol,—

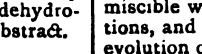


obtained by reducing methyltetrahydrobenzenemethylketone with sodium in moist ethereal solution, is a colourless oil, which boils at 195—200°, and has a smell very like that of menthol. It is insoluble in water, but is miscible with most of the ordinary solvents in all proportions, and it dissolves in concentrated hydriodic acid with evolution of heat,

The *acetate*, $C_6H_{10}Me{\cdot}CHMe{\cdot}OAc$, prepared by boiling the alcohol with acetic anhydride, is a colourless liquid boiling at 204—210°.

The *iodide*, $C_6H_{10}Me{\cdot}CHIMe$, is a heavy colourless liquid boiling at 178—180° (110 m.m.) and possessing a smell exactly like that of amyl iodide.

Orthomethyltetrahydrobenzenemethylcarbinol,—



is formed in small quantities in the preparation of orthomethylhexamethylenemethylcarbinol when the quantity of sodium employed is insufficient for complete reduction. It is a colourless liquid boiling at 141—143° (50 m.m.).

Orthomethylethylhexamethylene, $C_6H_{10}MeEt$, is obtained when methylhexamethylenemethylcarbinol is heated at 230—240° for four hours with a large excess of hydriodic acid of sp. gr. 1·96 and a little amorphous phosphorus. It is a colourless mobile liquid, with a smell closely resembling that of light petroleum, and boils at 150—152°.

The compound $C_{18}H_{26}O$ is obtained in the preparation of diacetylpentane and is formed by the condensation of two molecules of the diketone with elimination of three molecules of water; it is a very thick yellowish oil boiling at 265—275° (35 m.m.).

A condensation compound, $C_{18}H_{32}O_2$, is formed in the reduction of methyltetrahydrobenzenemethylketone; it is a thick yellowish oil, boiling at 255—265° (50 m.m.).

96. "*Action of Reducing Agents on α-ω-Diacetylpentane Formation of Dimethylheptamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

When α-ω-diacetylpentane is treated with excess of

sodium in moist ethereal solution, it is chiefly converted into orthodihydroxydimethylheptamethylene,—

$$CH_2\begin{<}CH_2\cdot CH_2\cdot CMe\cdot OH \\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{>}.$$

The same compound is formed when the diketone is reduced with sodium and alcohol at 80—100°. It is a thick colourless liquid, with a sharp, bitter taste, and a peculiar aromatic smell, rather like that of menthol. It boils at 201—202° (180 m.m.), is volatile with steam, and distils, seemingly without decomposition, at the ordinary temperature when heated in small quantities. It is sparingly soluble in cold water, but separates from the solution on warming or on adding sodium carbonate. It does not combine with sodium, hydrogen sulphite, nor with hydroxylamine in alkaline solution. The sodium-derivative, $C_7H_{10}Me_2(OH)\cdot ONa$, seems to crystallise with 1½ mols. H_2O, and is readily decomposed by water or when gently heated.

Orthodibromodimethylheptamethylene, $C_7H_{10}Br_2Me_2$, is obtained when the dihydroxy-compound is treated with excess of phosphoric bromide in chloroform solution. It is a yellowish mobile liquid, with an unpleasant, very irritating smell, and gradually decomposes on exposure to the air.

The *iodide*, $C_7H_{10}IMe_2\cdot OH$, can be prepared by boiling dihydroxydimethylheptamethylene with hydriodic acid of sp. gr. 1·96. It is a colourless oil, insoluble in water.

The diacetyl-derivative, $C_7H_{10}Me_2(OAc)_2$, prepared by boiling dihydroxydimethylheptamethylene with acetic anhydride, is a colourless mobile liquid, boiling at 199—202° (65 m.m.); it is readily hydrolysed by potash.

Orthodimethylheptamethylene, $C_7H_{12}Me_2$, is obtained, together with considerable quantities of a condensation product, when dihydroxydimethylheptamethylene is heated at 230—250° for eight hours with a large excess of hydriodic acid of sp. gr. 1·96, and a little amorphous phosphorus. It is a colourless mobile oil, boils at 150—152°, and has a smell not to be distinguished from that of light petroleum.

A compound, $C_{18}H_{34}O_3$, is formed in small quantities in the preparation of dihydroxydimethylheptamethylene; it is a very thick yellowish oil, boiling at 300—310° (200 m.m.).

97. "*Oxyamidosulphonates and their Conversion into Hyponitrites.*" By Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S.

The oxamidosulphonates are the sulphazidates of Fremy, which Claus and Raschig have shown to be monosulphonic-derivatives of hydroxylamine. A modification of Fremy's method of preparing the acids has been devised by the authors, dependent on their discovery of the existence of a neutral soluble barium salt in addition to that of the basic salt. They find that the sodium salt can only be prepared as a colourless, very viscid liquid, which does not solidify in the desiccator. The potassium salt is crystalline, but is not anhydrous, as stated by Claus.

The main interest of this paper lies in the behaviour of oxyamidosulphonates with strong alkalies, and with copper hydroxide. On treatment with alkali, instead of yielding sulphate and hydroxylamine, as asserted by Claus and Raschig:—

$$HO\cdot NH\cdot SO_3K + KOH = HONH_2 + K_2SO_4,$$

and as it is admitted they do when hydrolysed by an acid, the authors find that they are converted exclusively into sulphite and hyponitrite, thus—

$$2HO\cdot NH\cdot SO_3K + 4KOH = (KON)_2 + 2K_2SO_3 + 4OH_2;$$

this interaction affords much the most fruitful process known for converting nitrite into hyponitrite.

The reducing action of the sulphazidates was known even to Fremy, and has since been referred to the supposed conversion of the salts into hydroxylamine and sulphate, the hydroxylamine being supposed then to act on the copper hydroxide in the well-known way. The authors find in opposition to this belief that much sulphite as well as sulphate is formed, and that the cupric oxide reduced is only half that calculated on the above supposition. They would write the equation—

$$2HO\cdot NH\cdot SO_3K + 2CuO + 2KOH = \\ = K_2SO_3 + K_2SO_4 + Cu_2O + N_2O + 3H_2O,$$

and hold that it is the undisplaced hydrogen of ammonia only which in the salt acts directly as the reducing agent.

98. "*The Alloys of Lead, Tin, Zinc, and Cadmium.*" By A. P. Laurie.

In extension of his previous observations (*Trans.*, 1888, p. 88) the author has made voltaic cells with the various alloys and has thus compared their behaviour with that of the single metal by means of an electrometer. He concludes that the metals now examined do not combine together, thus confirming Matthiessen's conclusions.

PHYSICAL SOCIETY.

November 15, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Prof. J. Milne and Lieut. G. F. Eyre were elected Members.

Mr. Enright resumed the reading of his paper on the "*Electrification due to Contact of Gases with Liquids.*" Repeating his experiments with zinc and hydrochloric acid, the author, by passing the gas into an insulated metallic vessel connected with the electrometer, proved that it was always charged with electricity of the opposite kind to that of the solution.

The electrical phenomena of many other reactions have been investigated, with the result that the gas, whether H, CO_2, SO_3, SH_2, or Cl, is always electrified positively when escaping from acids, and negatively when leaving a solution of the salt. In some cases distinct reversal is not obtainable, but all these seem explicable by considering the solubility and power of diffusion of the resulting salts. Various other results given in the paper tend to confirm this hypothesis.

Seeking for an explanation of the observed phenomena, the author could arrive at no satisfactory one excepting "contact" between gases and liquids, and if this be the true explanation, he hoped to prove it directly by passing hydrogen through acid. In this, however, he was unsuccessful, owing, he believes, to the impossibility of bringing the gas into actual contact with the liquid. True contact only seems possible when the gas is in the nascent state. Some difficulty was experienced in obtaining non-electrified gas, for the charge is retained several hours after its production, even if the gas be kept in metallic vessels connected to earth. Such vessels, when recently filled, form condensers in which the electricity pervades an enclosed space, and whose charge is available on allowing the gas to escape. Soap-bubbles blown with newly generated hydrogen were also found to act as condensers, the liquid of which, when broken, exhibited a negative charge. This fact, the author suggested, may explain the so-called "fire-balls" sometimes seen during thunderstorms, for if by any abnormal distribution of heat a quantity of electrified air becomes enclosed by a film of moisture, its movements and behaviour would closely resemble those of fire-balls. A similar explanation was proposed for the phenomenon mentioned in a recent number of *Nature*, where part of a thundercloud was seen to separate from the mass, descend to earth, and rise again.

The latter part of the paper describes methods of measuring the contact potential differences between gases and liquids, the most satisfactory of which is a "water-dropper," and by its means the P.D. between hydrogen and hydrochloric acid was estimated to be about 42 volts.

Prof. Rücker asked if the experiment with zinc and hydrochloric acid could be started in the second stage by having the acid partly saturated with salt.

Dr. C. V. Burton thought it probable that contact could be made between a gas and a liquid by shaking them up together in a bottle.

In reply, Mr. Enright said the experiment could be started at any stage, and reversal effected as often as desired by adding either acid or a solution of salt to the generating vessel.

Mr. Herbert Tomlinson read a paper on the "*Effect of Repeated Heating and Cooling on the Electrical Resistance and Temperature-Coefficient of Annealed Iron.*"

In a paper recently presented to the Royal Society the author has brought forward an instance of an iron wire which, when subjected to magnetic cycles of minute range alternately at 17° and 100° C. had its molecular friction and magnetic permeability reduced respectively to about one-fourth and one-half their original values. The present experiments were undertaken to see whether by such heatings and coolings the temperature-coefficient of iron could be brought down to something approaching the number given by Matthiessen for "most pure metals." The wire experimented on was first annealed by heating to 1000° C. for several hours and allowing to cool slowly in a furnace placed at right angles to the magnetic meridian. The process was repeated three times. Afterwards the wire was covered with paper and wound doubly into a coil. This coil was enclosed in a water-jacketted air-chamber and connected with a sensitive Wheatstone bridge. Thermo-electric and Peltier effects were eliminated by always keeping the galvanometer circuit closed. By repeated heating to 100° C. and cooling to 17° C. for long intervals, the specific resistance at 17° C. was reduced from 11,162 to 10,688 C.G.S. units, after which the operations produced no further change; at the same time the temperature-coefficient increased in the proportion of 1 : 1·024. From careful determinations of the resistance at different temperatures the formula—

$$R_t = R_0(1+0{\cdot}005131t + 0{\cdot}00000815t^2)$$

was deduced, whilst that obtained from Matthiessen's results for pure iron annealed in hydrogen is—

$$R_c = R_0(1+0{\cdot}005425\,t+0{\cdot}0000083\,t^2).$$

Taking his own determination of specific resistance of impure iron as correct, coupled with Matthiessen's law connecting the resistances and temperature-coefficients of metals and their alloys, the author finds that the specific resistance of pure iron, deduced from Matthiessen's results, is from 4 to 5 per cent too high.

In conclusion, Mr. Tomlinson expresses a hope that the B.A. Electrical Standards Committee may be induced to determine the absolute resistance and temperature-coefficient of the pure metals which are in ordinary use.

Prof. Ayrton thought Matthiessen's results were expressed in B.A. units, and hence might appear one or two per cent too great. Mr. Tomlinson, however, believed the numbers he took were expressed in legal ohms.

Dr. Walmsley asked for what value of the magnetising force the permeability of the iron mentioned in the beginning of the paper was determined.

Mr. Tomlinson replied that they were much smaller than the earth's horizontal component.

Dr. Thompson's paper on "Geometrical Optics" was postponed.

OBITUARY.

Dr. GUSTAVE QUESNEVILLE.

We much regret having to put on record the death of Dr. Gustave Quesneville, which took place on the 14th inst. at his residence in the Rue de Buci, Paris.

The deceased has long occupied a prominent and honourable place in the scientific journalism of France. In 1840 he founded the *Revue Scientifique*, and conducted it until 1853. In 1857 he established the *Moniteur Scientifique*, which he has since edited, and which now ceases to appear. Our deceased colleague had reached the age of 80 years.

CORRESPONDENCE.

METAMORPHISM OF ROCKS.

To the Editor of the Chemical News.

Sir,—In the appreciative notice of my little work on the "Metamorphism of Rocks," which appeared in the Chemical News (vol. lx., p. 256), there are two points raised on which, in my prefatory note, I have not been quite clear.

1. The "outcry referred to" is not exactly that raised by Mr. A. Herbert's manifesto, with much of which I entirely sympathise, but the clamour for a "teaching university" in London to supersede or supplement the present university, which, so far from deserving much o the censure it has received, is, I think, deserving of more praise for *the* function it has fulfilled in the advancement of higher education in this country, setting up, as it does, a standard at once comprehensive and high for its *pass* degrees, instead of seeking to make itself a mere congeries of "finishing-schools" for young gentlemen.

2. I spoke of the academical career as a "race" *de facto*. It is not merely a "radical error," but the principle which vitiates English education more, perhaps, than anything else. It is one thing, however, to deprecate an evil, quite another thing to cure it; nor do I think there is much hope, for, so long as the present expensiveness of English university life is maintained, and the immoral trafficking in young brains, which underlies the scholarship system from the colleges at the universities down to the small preparatory school-boy of eight or nine, continues.—I am, &c.,

A. Irving.

Wellington College, Berks,
November 24, 1889.

WATER-BATH REGULATOR,

To the Editor of the Chemical News.

Sir,—It seems to me that the water-bath regulator described in the Chemical News (vol. lx., p. 250), could be made simpler still by doing away with the upper side-tube altogether, and passing the cold water in by the end of the tube figured as being open to the air.—I am, &c.,

"X."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 19, November 4, 1889.

On Phenyl Thiophene. — Adolphe Renard. — This compound forms brilliant white tablets melting at 170°, easily volatile, boiling about 330°. It is sparingly soluble in cold alcohol, more readily in hot alcohol, very soluble in benzene, petroleum essence, chloroform, carbon disulphide, less soluble in ether. It yields with isatin and sulphuric acid a blue solution, and with phenanthrenequinone and sulphuric acid a green colour. Its composition is expressed by the formula $C_6H_5-C_4H_3S$. If ox-

idised with chromic acid in an acetic solution it gives benzoic acid.

Researches on Digitaline and Tanghinine.— M. Arnaud.—The author assigns to digitaline the formula $C_{31}H_{50}O_{10}$, and to tanghinine $C_{27}H_{40}O_8$.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 40.

Report presented by H. Le Chatelier on behalf of the Committee of Chemical Arts on M. Candlot's work entitled "Practical Study on Portland Cement." —M. Candlot enumerates as the different methods now employed in the assay of cements:—Chemical analysis, measurement of the degree of fineness, determination of density, rapidity of setting, and determination of resistance to rupture. The composition of good cements does not vary widely. As a specimen of a good cement of average composition he gives:—Silica, 22·20; alumina, 6·72; iron oxide, 2·28; lime, 67·31; magnesia, 0·95; various, 0·66; total, 100·12. Any cement which deviates widely from this composition may be suspected, but one presenting a composition similar to the above is not necessarily good. A proportion of volatile matters (water and carbon dioxide) exceeding 3 per cent indicates an alteration from the action of air involving a decrease of resisting power. Matter insoluble in acids should not reach 1 per cent. An escape of hydrogen sulphide on the addition of an acid often indicates the fraudulent addition of blast-furnace slags. Chemical analysis, therefore, merely enables us to eliminate certain samples of bad quality, but it does not guarantee the good quality of others. *Fineness of Powder.* — The degree of fineness is measured by the quantity which does not pass through sieves of increasing grades of fineness; *e.g.*, No. 50 has 324 meshes per square centimetre, No 8 900, and No 200 5000. The degree of fineness is a useful datum, because granules which are too bulky do not become hydrated within, say, a month, but behave like inert sand. The proportion of grains which do not pass through the sieve of 5000 meshes should be reduced to a minimum. *Density.*—This datum varies widely according as we operate upon a single granule or upon a known volume of the powder. M. Candlot recommends that for determinations of density we should take only the portion which passes through sieves of 5000 meshes. Cements which have been well furnaced give 1·05 to 1·12; those badly furnaced, 0·93 to 1. *Duration of Setting.*—M. Candlot shows that the presence of foreign salts in the water modifies the time of setting. Calcium chloride, sulphate, and nitrate have a retarding influence; sodium chloride is inert. Sea-water has a strongly retarding influence as compared with fresh water. A sample of cement with fresh water set in twenty-five minutes; with sea-water in seven hours and a half; and with a one per cent solution of calcium chloride in ten hours. The rapidity of setting is an element too variable to furnish precise indications of the quality of a cement. M. Candlot considers that a useful cement should have the following properties:—(1) It should, when mixed with a suitable quantity of sand, present a sufficient resistance to a crushing pressure, but this resistance need not necessarily be very high. (2) The cement should possess a sufficient adhesiveness to ordinary building materials—brick and rough calcareous stones. (3) It must not become spontaneously disintegrated, split, or swell up, as occurs with samples containing free lime. (4). It must not become disintegrated under the influence of excessive atmospheric changes, such as dryness of the air or frost. (5) Cement for marine engineering works should resist as long as possible the action of magnesian salts.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. vi., No. 1.

Studies on the Processes of Analysis of the Raw Materials and the Products of Siderurgy.—Dr. M. C. Meinecke.—In this article the author speaks of the determination of sulphur in irons. He prefers the processes in which the hydrogen sulphide formed is converted into sulphuric acid by direct oxidation. As an oxidising agent he recommends alkaline oxygenated water, as used by Classen. The metal is dissolved in dilute hydrochloric acid (1 vol. acid at 1·19 sp. gr. and 1 vol. of water) in a flask holding 500 c.c., and connected with a continuous apparatus for generating hydrogen. The delivery-tube passes into a flask holding 250 c.c., in which the acid fumes are condensed and are then conveyed into two Volhard condensers, containing each 50 c.c. of oxygenated water at 2·5 per cent with 10 c.c. soda-lye (1 part pure sodium hydroxide dissolved in 3 parts of water). The metal is dissolved at first in the cold, and finally a gentle heat is applied.

Reduction of Ferric Bromide by Boiling its Solution.—L. L. de Koninck.—The products of the reaction are ferrous bromide and free bromine. The author considers that this reaction should be kept in view in operations where bromide is used as an oxidising agent in presence of iron.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Spermiciatia.—Can any correspondent tell me of a manufacturer in England of "spermiciatia?"—A Constant Reader.

MEETINGS FOR THE WEEK.

Monday, Dec. 2nd.—Medical, 8.30.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 3rd.—Institute of Civil Engineers, 8.
Wednesday, 4th.—Society of Arts, 8. "Rabies and its Prevention," by Armand Ruffer, M.A., M.D.
—— Geological, 8
Thursday, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8. Ballot for the Election of Fellows.
Friday, 6th.—Physical, 5. "The Electrification of a Steam Jet," by Shelford Bidwell, F.R.S. "Notes on Geometrical Optics," Part II., by Prof. S. P. Thompson, D.Sc. "On the Behaviour of Steel under Mechanical Stress," by C. H. Caras Wilson. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes.
—— Geologists' Association, 8.

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

VOL. LX. No. 1567.

A NEW, EASY, RAPID, AND CORRECT METHOD OF DETECTING TIN IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris).
Assistant to Professor of Geology and Mineralogy in the University of Edinburgh.

MINERALS containing tin yield, when mixed with fluxes and properly heated for some time before the blowpipe on charcoal in a good strong reducing flame, malleable metallic globules of a high lustre and silver-white colour. For the reduction of the ores of tin and most of the other minerals known to contain that metal, the common white flux or fusion-mixture of Fresenius ($K_2CO_3 + Na_2CO_3$) is quite adequate. In certain obstinate cases, however, it is advisable to use a little borax or potassium cyanide, or both, as well as fusion mixture. As the tin almost invariably, in the process of ordinary reduction on charcoal, separates out in rather small beads, which, because of their very fluid consistency at the temperature of the blowpipe flame, sink rapidly down through the flux, &c., to the bottom of the assay, or even a little distance into the support, it is necessary to cut out the ignited residue with some of the surrounding carbon on each side and below it, and transfer the whole to a mortar, where, after the operations, first of heavy and firm grinding to reduce the mixture to a fine powdery condition, and then of washing or lixiviating with water in order to remove everything of a non-metallic nature, have been gone through, the silver-like malleable scales of the metal will be observed mainly adhering to the bottom of the mortar, but in part also to the pounding extremity of the pestle.

To prove that these silvery scales are tin, throw over them, in the mortar, two or three drops of boiling concentrated hydrochloric acid, and then add, by means of a glass tube, one drop of a fairly strong water solution of gold chloride and swing the mixture of liquids all round the bottom of the mortar for about a minute. If the white metallic scales originally observed were composed wholly or partially of tin, then, by the treatment described, the bottom of the white porcelain or earthenware mortar will receive a distinct purple stain by the formation of the well-known characteristic purple of Cassius. To further confirm the presence of tin, allow a current of sulphuretted hydrogen gas to impinge for a very short time on the moist stained bottom of the mortar. The formation of a skin of brown stannous sulphide, arising from this action, will afford valuable additional and sufficient confirmation of the presence of the metal.

RATE OF DECOMPOSITION OF CHLORINE-WATER BY LIGHT.*

By Dr. G. GORE, F.R.S.

IN this research, the author has investigated, by means of the voltaic balance, the kind and amount of chemical change, the rate at which decomposition proceeds, and the chemical composition of the products formed at all stages of decomposition of chlorine-water when exposed to daylight and sunlight in colourless glass vessels.

The chlorine-water, by exposure to diffused daylight, was decomposed with moderate uniformity, but at a gradually diminishing rate, as shown by the losses of voltaic energy, until no further loss of such energy occurred; the liquid then consisted of an aqueous solution of hydrochloric acid, hydrochlorous acid, and chloric acid. By further exposure of the liquid to daylight and sunlight during several weeks, peroxide of hydrogen was formed, and the amount of hydrochloric acid and voltaic energy very slowly increased until that of the latter became equal to that of dilute hydrochloric acid of equivalent strength to the whole of the chlorine present; all the other chief properties of the final liquid agreed with those of a mixture of dilute hydrochloric acid and peroxide of hydrogen. Still further exposure to strong sunlight caused no further change in chemical composition, amount of voltaic energy, or other property of the liquid.

This research shows distinctly that the decomposition of chlorine-water by light may be divided into two essentially different parts, or periods, of chemical change, and that the kinds of chemical change occurring during these two periods are largely different. During the first period, a very great and gradual *loss* of voltaic energy occurs, attended by formation of hydrochloric, hydrochlorous, and chloric acids. During the second period, a moderate and very slow *increase* of voltaic energy takes place, accompanied by decomposition of the hydrochlorous and chloric acids; a further formation of hydrochloric acid, and the production of peroxide of hydrogen. Under the influence of prolonged sunlight, the whole of the oxygen of the hydrochlorous and chloric acids united with water to form peroxide of hydrogen, and the peroxide then combined with the whole of the hydrochloric acid to form a definite "solution compound," represented by the formula $2HCl.H_2O_2$.

The chemical composition of the products of the change at the end of the first and second periods were ascertained by means of the voltaic balance and ordinary chemical analysis. During the first period, forty consecutive measurements of the voltaic energy, at stated intervals of time, were made, and the energy diminished from about 12·19 millions to 2·9 millions; and during the second period, eight such measurements were made, and the energy increased to 9·3 millions. A curve is given showing the rate of loss of energy during the first period.

It is interesting to observe that suitably decomposed chlorine-water, or possibly, in its stead, a mixture of—

$$6HCl + HClO + HClO_3$$

in a proper proportion of water, has the property of absorbing energy by exposure to light, very much like that possessed by the green leaves of plants.

* Abstract of a Paper read before the Royal Society, June 20, 1889.

ON THE PREPARATION OF A STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION,

By WILLIAM FRENCH, A.I.C.

IN the course of practical instruction here, I have occasion frequently to prepare standard solutions of ferric salt for subsequent titration by the students; the method employed being previous reduction by Zn and H_2SO_4 and titration with $KMnO_4$.

The ferric salts available for such purpose, as sulphate, are, as a rule, impure and not always soluble, and therefore one has to titrate the solution after weighing the salt in order for the strength to be known. It occurred to me, however, to take a weighed quantity of ferrous ammonium sulphate, which can be obtained in a state of purity, dissolve in water, add a little sulphuric acid, and then hydrogen dioxide in small quantity; warm up, and finally boil, to expel excess of oxygen and decompose traces of H_2O_2.

I find this method works admirably, and the solution so obtained can be relied on as containing the iron put in, in

the ferric state, and needs no standardisation. The whole operation takes about half an hour.

University Chemical Laboratory,
Cambridge.

DETERMINATION OF TUNGSTEN IN METALLIC TUNGSTEN.

By ALFRED ZIEGLER.

In the *Chemiker Zeitung*, 1889, No. 36, is given a process by J. Preusser, which much abridges the determination of tungsten. He roasts the sifted metal in contact with air, and treats subsequently with aqua regia and hydrochloric acid, &c. The roasting, however, lasts for some hours, and cannot be executed in a platinum crucible, since tungsten attacks platinum, probably forming an alloy. It even leaves upon porcelain a permanent spot, perhaps imponderable, but enough to offend the eye of a conscientious chemist.

The author has succeeded in completing the roasting of tungsten in about three-quarters of an hour, as follows:—½ grm. of tungsten, finely ground in an agate mortar, is thrown upon ammonium nitrate melting at a low temperature in a platinum crucible (the ammonium salt must have been previously dehydrated by fusion). It is then heated until all the nitrate is driven off, leaving in the crucible the superficially oxidised metal, which, without injuring the crucible or the result, can be completely oxidised in a short time with a full Bunsen flame, stirring carefully with a stout platinum wire. The rest of the analysis is conducted in the usual manner.—*Chemiker Zeitung.*

ON THE QUALITATIVE ANALYSIS OF THE AMMONIUM SULPHIDE PRECIPITATE.

By F. MAYER.

In the first practical exercises in the laboratory it is well known that the separation of the ammonium sulphide precipitate presents various difficulties for the beginner.

Among the methods for examining this precipitate, separation with sodium acetate has been recently recommended as the simplest. This process rests upon the fact that, on boiling with sodium acetate, ferric oxide, and alumina in solutions as completely neutralised as possible are deposited respectively as basic acetate or as hydroxide, whilst salts of manganese and zinc remain in solution (nickel and cobalt are supposed to have been previously eliminated). In the absence of chromium compounds this separation, with due care, may be accurately and speedily effected; but not so in its presence, since chromium oxide by itself is not precipitated by boiling with sodium acetate, but in presence of ferric oxide it is sometimes precipitated and sometimes not, and occasionally it prevents the complete precipitation of the iron. The phenomena are similar to those which occur on adding potassium hydroxide to mixed solutions of ferric and chromic oxides.

From such solutions, however, ferric oxide and chromic oxide may be thrown down quantitatively by potassa if the former oxide is in excess as compared with the second (say 4 : 1). It seemed probable that this would also be the case in the sodium acetate method, and that a complete precipitation of the chrome might be effected by adding ferric chloride before boiling with sodium acetate. This conjecture has proved correct, and the author has thus succeeded in extending the sodium acetate method to chromiferous substances. About 5 atoms of iron are required for the precipitation of 1 atom of chrome on boiling with sodium acetate, and it is therefore needful to introduce the required quantity of ferric chloride into the solution without letting the excess become too great. The following is the best method of operating:—After dissolving the chromiferous ammonium sulphide precipitate in dilute hydrochloric acid and oxidising the solution with nitric acid, a small portion is tested for iron. In the absence of appreciable quantities of this metal the liquid is strongly diluted, the excess of acid removed by neutralisation, a little ferric chloride and sodium acetate are added, and a small specimen is boiled for a few minutes and filtered. If a sufficiency of iron was present or has been added the filtrate of this specimen is perfectly colourless, and does not turn yellow if warmed with hydrogen peroxide and caustic soda; a colour is produced by the formation of sodium chromate if any chrome compounds exist in the filtrate. (In presence of manganese compounds a second filtration must be performed to detect the colour). If chrome has been found in the filtrate, more ferric chloride is added to the main bulk until another small specimen shows the total precipitation of the chromium oxide. The whole quantity of liquid is then boiled for ten minutes and filtered. It is then certain that zinc and manganese remain in solution, whilst iron, aluminium, and chromium are quantitatively present in the precipitate.

In no case must the entire liquid mixed with sodium acetate be boiled until a sufficiency of ferric salt is present, since, as Reinitzer has observed and the author has confirmed, any chrome acetate, after boiling with ferric acetate, forms a so-called passive solution, from which neither chrome nor iron can be thrown down on a further addition of ferric chloride.

The precipitate is dried in the ordinary manner, fused with soda and saltpetre, and the alkaline chromate is extracted with water. Or the method proposed by Carnot (*Comptes Rendus*, cvii., p. 997) may be applied, which is, however, less advantageous.

In the simultaneous presence of chromium and phosphoric acid the sufficiency of the addition of ferric chloride must be ascertained not merely by the yellow precipitate given by soda-lye, but by the method indicated above (boiling with sodium acetate).

It is to be noted that if an equivalent quantity of a solution of aluminium was added in place of the iron, the chromium oxide was not completely precipitated. If a sufficiency of ferric chloride is present the chromium hydroxide is precipitated, even in presence of aluminium salts.

The hydrogen peroxide of commerce is sometimes completely useless for analytical purposes on account of such coarse impurities as barium chloride and salts of aluminium.—*Berichte d. Deutschen Chem. Gesellschaft* (vol. xxii., p. 2627).

MAGNESIUM BRONZE.

By H. N. WARREN, Research Analyst.

During the past week my attention having been drawn to the manufacture of magnesium bronze, I trust the following details may be observed with interest.

For the production of the various samples two ounces of metallic copper, contained in a graphite crucible, were raised to the melting-point by the aid of an injector-furnace, and upon its surface was projected half an ounce of magnesium metal; over this, melted borax was poured to prevent oxidation; the magnesium for a few moments burnt with intensity, the reaction quickly subsiding and proceeding tranquilly, emitting at intervals flashes of light characteristic of the metal. The crucible with its contents was now taken from the furnace, allowed to cool, and the metallic button extracted and examined as follows:—

The surface having been polished by the aid of fine sand, presented in appearance a highly zinciferous brass; on applying the hammer to the same, the ingot broke into various pieces, even under the influence of a slight stroke, and proved sufficiently brittle to be readily pulverised. Its solubility, oxidising properties, and fusing-point all closely resembled an ordinary brass. The analysis of the alloy showing 11 per cent magnesium; this was effected by dissolving the metal in nitric acid, precipitating the copper as oxide by means of soda, well washing the precipitate to free it from nitrates, and re-dissolving in hydrochloric acid, afterwards precipitating the whole of the copper by means of metallic magnesium. Washing the reduced copper thus obtained, and drying the same in an atmosphere of hydrogen; after cooling, weighing the metal, and calculating the difference to magnesium.

The remainder of the alloy was re-melted with the addition of various percentages of copper, and the former tests applied, the regulus becoming less brittle as the percentage of copper was increased, until an alloy containing 4 per cent magnesium was obtained, presenting in appearance a true bronze, and resembling the same as regards its physical properties, admitting of either being worked with the saw or readily turned. The experiments were further maintained until 1½ per cent of magnesium existed; this, although a small percentage, readily affected the copper, both by bleaching, and, to a certain extent, hardening the same. In short, the various alloys of copper and magnesium thus produced do not appear to excel, in general properties, the more common and, at the same time, more readily formed alloys of copper.

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THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

The Committee, having asked Mr. R. A. Hadfield to assist them in this investigation, beg leave to present the result of a series of experiments kindly undertaken by him.

Alloys of Iron and Silicon. By R. A. Hadfield.

The alloying of elements other than carbon with iron is a comparatively new field, and possesses special interest, not only to those concerned and engaged in the treatment of metals, but also to those who study the physical properties of substances. As the nature of alloys of carbon and iron is fairly well understood, it is hardly necessary to consider them here, and in order to narrow down the considerations dealt with in this paper to a practicable limit, attention will be confined solely to alloys or mixtures of which metallic iron and silicon form the principal constituents.

An investigation of the properties of manganese steel, *i.e.*, an alloy of iron and manganese, was placed before the Institution of Civil Engineers and Iron and Steel Institute by the author some twelve months ago, and its physical properties have been fairly well determined as compared with alloys of iron with other elements. This was the more practicable owing to the fact that the manufacture of "cast-iron" alloys of manganese—that is, ferro-manganese, has been for some time past in a very advanced state. In other words, by the cheap production of the alloys known as rich ferro-manganese—a material containing 80 per cent of ferro-manganese, 5 per cent to 7 per cent of carbon, and the rest iron, has enabled experiments to be readily carried out by further alloying such rich manganese products with pure iron.

Mr. Turner's paper, read before this Association at Bath last year, described experiments with steel containing from 0·10 per cent to 0·50 per cent silicon, and the details were fully given in the *Transactions*. The writer was asked by Mr. Turner and your Committee to investigate the effect of higher percentages of silicon.

The subject of alloys of iron and silicon has for some years occupied the writer's attention, but it is only lately that rich cast-iron alloys of silicon, *i.e.*, ferro-silicon, have been obtainable; and even now they cannot compare in richness of silicon with that of the manganese in ferro-manganese. The highest ferro-silicon yet made contains not more than about 18 per cent to 20 per cent of silicon. Fortunately, however, owing to the peculiar fact, noticed more fully further on, as to its lowness in carbon, this is much better fitted for experimental work as compared with, say, 20 per cent ferro-manganese. Such percentage of silicon, though, comparatively speaking, not so high, is sufficient to enable a suitable experimental material to be made, *i.e.*, a resultant material not containing too much carbon to interfere with an examination of the effect of the metalloid silicon upon the metal iron. Thus, while in the case of rich spiegel or ferro-manganese the carbon present amounts to some 5 per cent or 6 per cent, the 20 per cent ferro-silicon, on the contrary, contains comparatively little carbon—always under 1½ per cent, and often under ¾ per cent; so that by means of this cast-iron alloy, when further diluted or mixed with pure iron, the malleable material or steel produced practically contains but little carbon. The curious fact that ferro-silicon alloys as they rise in silicon diminish in carbon, was first noticed in some laboratory experiments eighteen years ago by Mr. Edward Riley; this will be again referred to further on. Whilst the scope of the experiments described in the present paper is in no way to deal with material other than malleable compounds of iron and silicon with small quantities of iron and manganese, it may be useful to give some general reference to previous experiments.

The only commercial employment of silicon with other metals is that of silicon bronzes. It is stated to act upon the copper in a similar manner to phosphorus. The qualities of such alloys are great strength and tenacity, high electrical conductivity, and resistance to corrosion. Wire made of this material is stated to have a conductivity of 80 per cent, and a tensile strength of about 36 tons per square inch.

Mr. Warren, in a recent number of the Chemical News, states that silicon, when in the nascent state, converts platinum into a brittle silicide; or, by heating graphitoidal silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus containing as high as 10 per cent silicon, which is fusible at a red heat, and breaks with a crystalline fracture.

Silver and gold are reported as not presenting any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride with either silver or gold in an amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance an alloy containing 5 per cent of silicon is almost as brittle as antimony. Silver, when alloyed with 10 per cent of silicon is stated to have a slightly red tint.

Rich cast-iron alloys of silicon are now usually described respectively as ferro-silicon and silicon-spiegel, the latter containing manganese in addition to silicon. Siliceous alloys of cast-iron were usually known as glazed pigs, owing to their peculiar glazed appearance when fractured. It is curious that this very material—burnt pig, as it was often called, and only then made accidentally—was formerly thrown on one side as useless, whereas now it is made purposely on a commercial scale and in large quantities—another of the many proofs of the advantage of bringing scientific knowledge to bear upon industrial metallurgy. Such ferro-silicon in itself

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B, Newcastle Meeting.

alone is perfectly useless in the refinery or puddling furnace or for iron castings. The early samples of siliceous iron seldom contained more than from 4 per cent to 6 per cent of silicon; But Mr. Riley, of London, in 1872, was the first to point out that rich ferro silicon was likely to play an important part in metallurgical industry. By means of laboratory experiments, he made in the crucible samples containing as high as 22 per cent of silicon. He also discovered that as silicon increased carbon decreased, until with 20 per cent of the former the latter was not present in quantities of more than $\frac{3}{4}$ per cent to 1 per cent, and the greater part of this small amount existed as graphite. Spiegeleisen and ferro-manganese are the richest carbon alloys that can be produced, and they contain about 6 per cent of carbon; ordinary cast-iron rarely exceeds more than about 4 per cent, and never more than about $4\frac{1}{2}$ per cent. So strong, however, is the action of silicon in preventing carbonisation, even in the presence of a large excess of carbonaceous fuel, that in silicon-spiegel, an alloy of iron, manganese, silicon, and carbon, and notwithstanding the presence of a large amount of manganese, it—that is, the silicon—had still the upper hand, and prevents, as in the case of ferro-silicon, carbonisation taking place. A few typical analyses of ferro-silicon, silicon-spiegel, ferro-manganese, and spiegeleisen may be of interest here (see Table I.); for a fuller description, and for the methods of manufacture employed in their production, reference is given to Mr. Holgate's admirable paper on "The Composition of Ferro-Manganese and Ferro-Silicon made in the Blast Furnace." The writer is indebted to that paper for the analyses in question. Four of the samples quoted represent spiegel and ferro-manganese; and it is interesting to note that as the manganese rises there is a gradual increase of carbon up to as high as 7 per cent. A noteworthy fact is that if silicon, even in 50 per cent ferro-manganese, is allowed to reach 4 per cent the carbon is at once much reduced, in some cases to the low amount of about $2\frac{1}{2}$ per cent. This action is still more intensified in the alloys known as silicon-spiegel or silicide of manganese, of which two analyses are given. From the latter it will be seen that, provided the silicon exceeds 10 per cent, the carbon is reduced to an exceedingly low point, and that although manganese may be present even in comparatively high percentages this is quite immaterial. This decrease of carbon takes place both in the combined and graphitic form, but principally in the former. A very valuable property of these spiegel alloys is the fact that they contain practically no sulphur, the much-dreaded enemy of the steel maker.

TABLE I.—*Analyses of Spiegel, Ferro-Manganese, Silicon-Spiegel, and Ferro-Silicon.*

	Analysis per cent.			
	Carbon.			
	Graphite.	Combined.	Silicon.	Manganese.
Analyses of spiegel and ferro-manganese, showing the gradual increase of carbon as the manganese increases.	—	4·27	0·110	8·11
	—	4·78	0·52	19·74
	—	5·63	0·42	41·82
	—	6·53	0·97	80·04
	—	7·20	0·14	80·04
Analyses of special manganese, showing that if the silicon becomes high the carbon diminishes very considerably.	—	3·56	4·90	23·90
	—	2·56	4·20	50·00
Analyses of silicon-spiegel or silicide of manganese.	0·33	1·85	10·74	19·64
	0·67	0·98	12·60	19 74
	0·90	0·30	15·94	24·36
Analyses of ferro-silicon.	2·35	0·05	8·77	2·42
	1·85	0·06	11·20	2·78
	1·20	0·23	14·00	1·95
	0·55	0·11	17·80	1·07

Remarks.—Sulphur and phosphorus practically absent, remainder being iron.

NOTE.—These Analyses are from the paper of Mr. Holgate, Assoc.R S.M. Darwen, on "The Manufacture of Ferro-Manganese and Ferro-Silicon in the Blast-Furnace."

It will therefore be seen that in the blast-furnace, somewhat strange to say, silicon cannot be reduced without carbon is also present; yet, when reduction of silicon occurs with the production of highly siliceous iron, carbon is practically absent in the resultant material. The late Dr. Percy, more than twenty years ago, referred to this in his "Metallurgy," and said that according to his experience no reduction can take place when silica and iron, without carbon, are heated together, even at the highest furnace temperature. Possibly this might now be accomplished in the powerful electric smelting furnaces, and it would be interesting to know whether alloys as rich in silicon as are the present valuable alloys of ferro-manganese rich in manganese could be produced. If so, without doubt, considerable employment could be found for them in metallurgical industry.

Alloys or compounds of iron, carbon, and silicon, non-malleable in their nature, and coming under the term "cast-iron," have been thoroughly investigated in this country by Mr. T. Turner, of Birmingham, the Secretary of our B.A. Committee, and the results placed before the Iron and Steel Institute, so that it is unnecessary to do more than touch upon this matter here. Great credit is due to this investigator for the lengthy and valuable researches he has made in this direction, as also to Mr. Keep, of Detroit, U.S.A., who has lately presented interesting papers on the same subject to the American Institute of Mining Engineers. Mr. Keep sums up so well the general results of all investigations up to date, that it may be well to briefly mention them, especially as some of the remarks apply to a great extent to the malleable compounds or alloys of iron or silicon now being described. Both Mr. Keep and Mr. Turner find that white carbonaceous cast-iron, which would invariably give porous and brittle castings, are made free from honeycombs, and possess much greater strength by the addition of comparatively small amounts of silicon: the latter result as to gain in strength is one which was considered contrary to previous experience. If further additions are made, say up to 2 per cent, the iron becomes grey, and at this point the maximum strength is obtained. If more silicon is added, although the iron becomes still more grey it also becomes weaker. By a still further addition a closer grain results, but it is even more brittle than in its white condition. Too much silicon also produces, as in the silicon steel now being described, lack of fluidity and greater shrinkage. Mr. Keep thinks that silicon in cast-iron is evidently, to some extent, combined with the iron and carbon; but whether it exists also in the form corresponding with graphitic carbon, mechanically mixed with the remaining mass, is a question still in dispute and unanswered. As now well known, the principal effect of silicon is to change the carbon from the combined to the graphitic state. One point particularly mentioned by Mr. Keep, and an important one, is that silicon irons have always had the reputation of imparting fluidity to other brands; and naturally this was at first supposed to be owing to the silicon added. It has now been found that this is not directly so, and that it is merely from the fact that the silicon present causes an increase in the quantity of graphite, and consequently a more fluid cast-iron. It is not, therefore, directly the cause except by its indirect action on the carbon.

In conclusion on this point, Mr. Snelus said, more than seventeen years ago, it is generally supposed that the absorption of much silicon tends to set free the carbon in the graphitic state. No statement more concisely expresses the influence of silicon on what is termed cast-

iron than that given some eight years ago by Mr. C. F. King, of Newport, U.S.A., in an able paper read before the American Institute of Mining Engineers on "The Chemical Action of the Bessemer Process." He said it is due to the presence of silicon in pig-iron that carbon is set free on cooling, and it is in proportion to the elimination of the silicon that the carbon remains chemically combined. Mr. King gives a diagram showing the rate of elimination of the metalloids in the process named, and it is a somewhat remarkable coincidence that the percentage point (1·8 per cent silicon), where the diminishing silicon curve cuts the combined carbon and graphitic curves, is exactly that which gave the maximum tensile strength in the material made by Mr. T. Turner, and later by Mr. Keep, in their numerous tests as to the effect of silicon upon cast-iron. The diagram referred to shows that by a diminution in the silicon highly graphitic pig-iron becomes rapidly mottled, and eventually white, although, practically, none or but little total carbon is oxidised, and this, as far as can be seen, solely by the fall of the silicon from 2·50 to 1·70 per cent. Whilst, therefore, Messrs. Turner and Keep show that white iron can be converted into mottled, and eventually grey, by means of additions of silicon, this diagram shows the converse, namely, that with silicon abstracted grey cast-iron becomes mottled and eventually white.

(To be continued).

SOME CONSIDERATIONS IN REGARD TO THE FORMATION OF COAL AND CARBONACEOUS MINERALS.

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(Concluded from p. 264).

Cannel used alone in gas-making, as in Edinburgh and Glasgow, gives a tar yielding less benzine and its homologues than that from bituminous coal, and these are mixed with a notable proportion of fatty hydrocarbons. From this tar olefins and paraffins boiling from 20° to 100° C. are obtainable, and of the liquid obtained at the boiling-point of benzine, only about two-thirds consist of that substance which crystallises out when the mixture is placed in ice and salt. On distilling cannel tar only about ten per cent of oils are obtained, which are lighter than water, about thirty-five per cent on the tar being heavier, and although the lower fractions contain notable quantities of fatty hydrocarbons, these gradually decrease until the heavy pitch-oil contains mere traces of paraffins. I speak here of the low heats used in gas-making thirty years since; with the high heats employed now-a-days the quantity of light hydrocarbons is much smaller, not above four to five per cent. On the other hand, cannel has been little used for low temperature work (except Leeswood cannel, which was what we would call here kerosene shale), although the amount of volatile hydrocarbons it contains ranges from forty to forty-five per cent, and even higher in Scotch cannels, where shales yielding thirteen per cent of oil are worked. Cannel oil in my experience is troublesome to purify, yielding much tar (polyminerised acetylenes, &c.) to sulphuric acid.

Shale is very rarely used alone for making gas, but it is so used for the gas for the railway carriages on our Government railways. I tried to procure a sample of the tar, but found that unfortunately it could not be kept separate from the tar from bituminous coal, from which gas is also made. The mixed tar was just heavier than water, and particularly mobile for a tar. Subjected to distillation, the process being carried so far that the residue in the retort set to a rather hard pitch on cooling, it gave a distillate wholly lighter than water. This distillate treated by reagents gave the following percentages by bulk:—

8·5 per cent to concentrated sulphuric acid—basic bodies and polyminerised acetylenes.
31·9 per cent sodium hydrate—phenols—and conjugate acid bodies formed by previous treatment with acid.
46·7 per cent to nitric acid—aromatic hydrocarbons and olefins.
12·7 per cent unattacked—paraffins.

99·8

As the shale used gives on low temperature-distillation a refined product containing paraffins to olefins in the ratio of 3 to 7, the 12·7 per cent above would give 29·6 per cent of olefins, which, added to 12·7, gives 42·3 per cent of fatty hydrocarbons, and subtracted from 46·7 gives 17·1 per cent of aromatic. If we consider that the amount of phenols extracted by soda from coal-tar is about 6 per cent, and this added at the same rate to the 17·1 per cent of aromatic hydrocarbon, would give 18·2 per cent of coal-tar hydrocarbons, and we would then have 18·2 coal hydrocarbons to 42·3 of fatty or shale hydrocarbons, which is in the ratio of 1 to 2·32. I am informed by Mr. Inspector Mitchell that the quantities of material used in the gas works are 9⅛ tons of Newcastle coal and 7⅛ tons shale per week, and as coal gives approximately 10 gallons of tar per ton, whilst shale averages about 27 gallons, this would give the following ratios:—

Coal to shale as 1 : 0·82
Coal-tar to shale-tar as 1 : 2·29

which shows a tolerably close approach to the ratio of hydrocarbons actually found. In this only the more stable hydrocarbons which have been taken into consideration; but, look at the matter how we may, there seems no doubt that the fatty hydrocarbons remain true to their type, and are much less readily converted into the higher carbon aromatics than is usually assumed under the conditions of high temperature-distillation as carried out on a large scale. This is further shown in the fact that although numbers of inventors have proposed processes, and have taken out patents for the conversion of the comparatively low value fatty hydrocarbons into the higher value aromatic ones by passing the vapours through heated tubes and otherwise, none of these have been commercially successful in consequence of the loss being great in the form of lower fatty hydrocarbons, and the yield of aromatic therefore small.

The C_6 formula of cellulose has been thought to connect it with the aromatic series, but all transformations convert it into hydrocarbons, alcohols, and acids of the fatty series. On the other hand, ligno-cellulose, as found in jute and other bast fibres with a higher percentage of carbon and a lower of oxygen, does yield aromatic compounds—as hippuric acid during its digestion by herbivora — and by its giving pyrocatechuic acid by chlorination, and subsequent treatment of the chlorinated product by fusion with potash. Ligno-cellulose, however, treated with nitric and sulphuric acid, yields no aromatic nitro-derivatives, so that the benzine nucleus must be absent. This seems to connect ligno-cellulose with these coals, which do not yield valuable aromatics during distillation, that is, cokeing, steam, and splint. I do not enter further into the consideration of those coals at present.

Suberose, cutose, or adipo-cellulose, the principal constituent of cork and the cuticular envelopes of plant tissues, differs widely from ordinary cellulose, and yields, by all treatments, substances belonging to the fatty series, and it seems probable that if transformed into mineral coal it would retain its fatty character.

Published analyses of these three celluloses show the following numbers:—

	Cellulose.	Ligno-cellulose.	Apido-cellulose.
Carbon	44·6	47·0	73·66
Hydrogen ..	6·3	6·0	11·37
Oxygen	49·7	47·0	14·97

I shall now refer to the three varieties of coal usually subjected to distillation for their products, and shall take first bituminous coal, used for gas-making and yielding valuable aromatic hydrocarbons as a by-product. The published analyses of coals are of little value for comparison for the purpose in hand, as these analyses have been made from average samples of different seams to determine their commercial value, and so do not take into account the fact that almost every coal is made up of a mixture of heterogeneous materials varying from nearly pure carbon to substances containing large percentages of hydrogen and oxygen. Even in the different bands, into which coal seams are divided by partings, the average of each band may differ very considerably from the average of the whole. Thus in the six bands of a coal seam which I recently examined, the ratio of volatile hydrocarbon to fixed carbon was in each band.

No. 1..	1 : 1·977
„ 2..	1 : 2·750
„ 3..	1 : 2·349
„ 4..	1 : 3·075
„ 5..	1 : 2·260
„ 6..	1 : 1·122

It appears doubtful whether much information could be got from making ultimate analyses of the separated constituents of any coal (except in the case of the substance No. 1 below, which I shall examine further), and I have confined myself to determining the hydrocarbons driven off at a cherry-red heat from different materials in the same block of coal.

In some Newcastle coal, colliery unknown, a piece was separated into jet-black bituminous matter, which broke easily into more or less cubical fragments, and a dense hard coal with a rather pale lustre. Subjected to heat the bituminous portion fused together, forming a swollen bright coke, whilst the other did not fuse, but shrank slightly, and gave a coke of the same shape as the original, or nearly so, and silvery. The ratio of volatile matters to fixed carbon was—

	Volatile.		Fixed carbon.	Ash.
In No. 1 ..	1	:	2·012	0·52 per cent.
„ 2 ..	1	:	3·455	9·81 „

The ash in No. 1 was composed almost entirely of ferric oxide; that of No. 2 was greyish.

A piece of Stockton coal, which is considered one of the best of our Newcastle coals for gas-making, similar in appearance to the first, gave—

	Volatile.		Fixed carbon.	Ash.
No. 3 ..	1	:	1·870	1·12 per cent.

In this case also the ash was almost entirely composed of oxide of iron. This coal is bituminous to such an extent that I could not get enough non-bituminous to examine by itself.

The coals of our Western districts are much less bituminous than in the Northern, and the bituminous matter is in very thin layers. From No. 4, the bright black portion of a piece of Lithgow Valley coal, and from No. 5, the contiguous dull portion, I got—

	Volatile.		Fixed carbon.	Ash.
No. 4 ..	1	:	1·889	1·07 per cent.
„ 5 ..	1	:	2·248	5·63 „

No. 4 swelled up and united into a single mass, but did not so entirely lose its original outline as in the case of No. 1, and it was lustrous black, not silvery. The ash consisted chiefly of alumina with a little oxide of iron and some traces of silica.

In No. 5 the coke was shrunk, and of the same shape as the coal. There were some bright black thread-like bands in No. 5 which it was impossible to remove, and these probably raised the percentage of volatile matter. I could not avoid this, as I wished to have the portions of coal immediately contiguous.

Those results seem to indicate that the bituminous part arises from altered resin, from the low ratio of fixed carbon, and the low percentage of ash; in the case of those from Newcastle, oxide of iron, which could be introduced by infiltration, as could also be the case with the alumina in the Lithgow Valley, as the water of the overlying Hawkesbury Sandstone generally contains sulphate of alumina in solution.

In connection with a coal from Mittagong, the analysis of which was published in the "Annual Report of the Department of Mines," in 1878, I made the following remark, which has been reproduced in Professor Liversidge's "Minerals of New South Wales":—

"The bright lines of fracture were marked by numerous lens-shaped cavities 0·05 to 0·10 inch in greater diameter, generally filled with a brownish pulverulent carbonaceous matter. These were apparently the impressions and remains of seeds, and they showed traces of a dense cortical layer. The bituminous matter on heating glowed, emitted a smoky odour, and burned away completely."

These seeds were quite absent except in the bright layers. Now if the seeds fell and were enclosed in resin, germination would be prevented and they would be preserved, whilst if they fell in decaying vegetable matter all traces of them would be lost.

I conclude, therefore, that the bituminous coals yielding low and valuable hydrocarbons on distillation are originally derived from aromatic resin bearing plants, the resinous ligno-cellulose of which contributed to the result; whilst the cambium or more cellulosic portions were mostly lost by decay, a little being converted into mineral charcoal. We can see the preservation of resin in retinite and also in the more recent Kauri and grass-tree gums, where the cellulose has often disappeared.

Cannel.—I have no analysis of my own of this mineral, but give below the ratio of volatile matter and fixed carbons from two analyses given in Percy's "Fuel" and one from "Watts's Dictionary." In nearly all books analyses of true cannels are mixed up with those of torbanite or kerosene shale from Bathgate and elsewhere.

The Lesmahagow is a true typical cannel from the middle ward of Lanarkshire, and there called candle coal (pronounced caun'l), where it was first used to give light in the farmhouse kitchens, a lump being put on the red fire in the evening.

	Volatile.		Fixed carbon.	Ash.
Lesmahagow ..	1	:	1·495	6·03 per cent.
Wigan	1	:	1·304	2·40 „
Mold	1	:	1·188	—

Cannel differs from bituminous coal in being of a nearly uniform texture, in which it resembles torbanite, but differs from the latter in every other way. From the character of the hydrocarbons it yields on distillation, it seems probably derived from adipo-cellulose, and ligno-cellulose, the former having considerable development in plants, which, from the comparative uniformity of the mineral, were probably of small size.

Torbanite or Kerosene Shale.—In the coals and cannels the volatile hydrocarbons are always less than the fixed carbon, whilst in the shales this ratio is always reversed and that irrespective of the amount of ash present. The following are five recent determinations of mine, the carbon being the smaller is taken as No. 1, not the volatile matter as in the coals:—

	Carbon.	Volatile hydrocarbon.	Ash.
No. 1. Joadja Creek.. ..	1 :	16·908	6·17
„ 2. Source unknown ..	1 :	12·500	6·20
„ 3. Murrurundi	1 :	8·625	21·32
„ 4. „	1 :	6·041	40·88
„ 5. United States ..	1 :	2·561	7·95

Nos. 1 and 2 were beautiful fine-grained shales, with a velvety lustre and pale streak.

No. 3, fine-grained brownish, scarcely velvety.

No. 4, coarse-grained brownish, dull.

No. 5, black, dull—streak dark brown, almost black.

It will be observed that the ratios in these shales differ widely, and also that the percentage of ash has a great range, but the value of the shale for distillation, either for oil or gas, appears to depend more on the ratio of hydrocarbons to fixed carbon than upon the quantity of ash. Thus, No. 3 is a shale much superior, whilst No. 4 is very little inferior to No. 5, although it contains more than five times as much ash. I refer to the quantity of gas or oil yielded. If distilled for oil, No. 5 would yield a very bad quality, the distillate containing much tar. This shale approaches in appearance the outlying portions of the better shales where they have been pinched under heavy cover.

Looking at the ultimate composition of shale in conjunction with the yield of fatty hydrocarbons, I was at first inclined to consider it as a product of adipo-cellulose. The following are analyses—first, of torbanite from Bathgate given in "Watts's Dictionary"; second, of shale from Hartley, by Professor Liversidge, which I have calculated free from ash, and for comparison I repeat that of adipo-celluloses in the third column.

	I.	II.	III.
Carbon	79·6	79·67	73·66
Hydrogen..	11·2	12·92	11·37
Oxygen, nitrogen, and sulphur* ..	9·1	7·41	14·97
	99·9	100·00	100·00

I subjected some carefully selected cork in thin shavings as the nearest substitute for adipo-cellulose to a rapid red heat and also pure cellulose, and obtained the following ratios:—

	Fixed carbon.	Volatile matter.
Cork..	1 :	5·245
Cellulose.. ..	1 :	7·916

As under no conceivable conditions could the ratio of volatile matter be increased during the conversion into mineral, the similarity in composition goes for nothing.

It has been suggested by someone that the shales are the products of resinous spores of some plant. From the persistent fatty products of distillation I think resin must be abandoned as resins pass more to aromatics. It appears to me more probable that shale comes from some oil or wax producing plant, more likely the latter, in view of the considerable yield of solid paraffin.

The shale at Joadja Creek is very uniform in texture: there is here and there a star-like speck of so-called jet, and rarely a ribbon-like piece of the same running through a block, perhaps an inch or so wide and barely an eighth of an inch thick. As there is bituminous coal above, these may represent resinous roots, but I could not get any for examination in time for this paper. At Joadja there is a ligno-cellulose coal below, a wax shale in the middle, and a resinous ligno-cellulose coal above.

Several other points have occurred to me since I promised this paper for the meeting of the Association, but pressure of other work has prevented me going into them.

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* The sulphur and nitrogen are very small in these shales. The only difference is an increase of carbon and a decrease of oxygen in the shales.

Addendum, September 29.—Since writing the above paper I have found in my notes an analysis of the best Joadja Creek shale, for which I had before looked in vain. In the first column is given the analysis; in the second the carbon, hydrogen, and oxygen only, eliminating the other ingredients as extraneous; in the third the numbers for the formula $C_{34}H_{64}O_2$, that is, a paraffin with 4H replaced by 2O (calculated).

	I.	II.	III.
Carbon	75·32	81·10	C_{34} 80·95
Hydrogen	12·05	12·97	H_{64} 12·69
Oxygen	5·49	5·93	O_2 6·33
Nitrogen	0·28	—	—
Sulphur	0·31	—	—
Ash	6·55	—	—
	100·00	100·00	

Pyrites was observed in the shale and was probably the source of the sulphur.

I do not attach much importance to the formula obtained, as the organic matter of shale is not a pure substance, though I think an approach thereto. For comparison there are given below some analyses of waxes. First, myricin or myricyl-palmatate (calculated); second, ceroxylin or palm wax, the average of three analysis by Boussingault, Lewy, and Teschemacher ("Watts's Dictionary," i., 837); third, carnabau wax by Lewy ("Watts's Dictionary," i., 805); fourth, occuba wax by Lewy ("Watts's Dictionary," iv., 173); and fifth, tristearin (calculated).

	I.	II.	II.	IV.	V.
Carbon	79·31	80·74	80·30	74·0	76·8
Hydrogen ..	13·22	13·26	13·00	11·3	12·3
Oxygen.. ..	7·47	7·00	6·70	14·7	10·9

Occuba wax (No. 4), the product of a plant growing in marshy places in South America, is not a true wax, but a mixture of solid fats.

It seems evident that the organic matter of shale, if produced, as I think probable, from a vegetable secretion, must have been so produced by the elimination of hydrogen and oxygen in the form of water, with probably elimination of hydrogen also by atmospheric oxygen, and could not arise from either of the last two, which contain less hydrogen, and still less could it arise from fats of lower molecular weight than tristearin, whilst it is possible from the waxes. This is more clearly seen if in Nos. 4 and 5 the hydrogen and oxygen are calculated for a quantity of carbon equal to that in the shale, thus:—

	IV.	V.
Carbon (as in shale)	81·10	81·10
Hydrogen	12·39	12·98
Oxygen..	16·11	11·52

The first shows less hydrogen than the shale, the last an equal quantity, but in both there is a large percentage of oxygen to remove hydrogen, which is not the case with the waxes, in which indeed the oxygen is rather deficient, which deficiency could be supplied by atmospheric oxygen.

The objection to derivation from fats apply with even greater force to the derivation from amber (succinite) and similar mineral resins, probably little altered in constitution, a connection claimed by Dana in Bathvillite ("Mineralogy," p. 742), as amber contains much less hydrogen than Bathvillite or shale.

The organic matter of the shale of this country is evidently a very stable body. It is almost absolutely insoluble in naphtha, carbon bisulphide, and similar menstrua. It is scarcely acted on by exposure to the weather, as for years subjected to fierce sun in summer, frost in winter, and rain at all times, it only becomes slightly brown on the immediate surface. Long continued

boiling with caustic alkali dissolves from the powder, only a trace of humus-like matter and fusion with caustic potash for two hours gives a similar result, whilst amber is soluble in alkalies. The bituminous matter of coal is insoluble in solution of caustic potash, but fusion with potassium hydrate renders it largely soluble in water. In this respect it is different from the "jet" mentioned above, which is insoluble in such menstrua as carbon bisulphide, &c., in caustic potash solution, and long fusion with caustic potash gives no more soluble matter than is obtained from the shale itself,

This "jet" subjected quickly to a cherry-red heat gives—

Volatile matter	41·12
Carbon*	55·80
Ash	3·08

The ash was reddish-coloured from the presence of oxide of iron. The immediately adjacent shale gave 9·16 per cent of white ash, whilst the volatile matter was 83·62 per cent and the fixed carbon 7·21, indicating a radically different original constitution from the jet, although in some respects that was different from the bituminous matter of coal.—*Proceedings of Australasian Association for the Advancement of Science*, Sydney, 1888.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Munro Taylor Anderson, Edgar House, Combs, Suffolk; George Frederick Brindley, Aluminium Company, Oldbury, near Birmingham; Philip Howard Davis, 106, Talcott Road, S.W.; Alexander Charles Farquharson, 13, Stonebyres Terrace, Partick, Glasgow; P. J. Hartog, 6, Greville Road, London, N.W.; Robert Law, 70, Maxwell Road, Pollokshields, Glasgow; Hugh Marshall, 1, Lorne Terrace, Edinburgh; Francis Herbert Mason, Outalpa, Harlesden, N.W.; Edgar Philip Penman, B.Sc., 32, Oakington Road, Elgin Avenue, W.; Edward Russell, 75, Kelvin Road, Highbury Park, N.; Henry Heron Smith, Wilton House, Vicarage Park, Plumstead, S.E.; John Wade, 129, High Road, Lee, S.E.

The following papers were read:—

99. "*The Law of the Freezing-points of Solutions.*" By S. U. Pickering.

Although the influence which a substance exerts in lowering the freezing point of a solvent, when used with caution, may give valuable evidence as to its molecular weight in the quasi-gaseous condition, it is impossible to accept Raoult's statement of the observed facts as a general law of freezing-points. The so-called constant exhibits a variation of some 20 or 30 per cent in the case of different substances (not counting those cases where the values are admittedly abnormal), and may also vary to the same, or to a greater, extent, when different proportions of the same substance and solvent are taken, even when we confine our attention to cases where the proportion is that of not more than 1 mol. to 100 mols. of the solvent. Still less can we, on the strength of the supposed constancy of the value, draw any conclusion from it respecting the nature of solutions.

The author believes that he has found the law which regulates the freezing-point of a solution of any strength. He attributes the lowering produced by the dissolved substance to three distinct causes, which he classifies as (1) mechanical, (2) physical, and (3) chemical.

* The carbon was left as a highly intumesced bright coke.

In the first place, he points out that if a weak solution (taking water as a concrete instance of a solvent) consists, as he maintains it does, of a hydrate, the water which crystallises out on cooling is derived from the hydrate itself; which is thermally possible, since the heat of solidification of the water is far in excess of the heat of formation of the hydrate. Hence the whole hydrate does not act as the "foreign molecule," but only that part of it which is not water, *e.g.*, H_2SO_4; and hence, also, the molecular weight obtained by Raoult's method is that of the H_2SO_4, and not that of the hydrate. But, although the decomposition of a complex hydrate into the next lower one and solid water is an exothermic change, such would not be the case with all the lower hydrates, and, in fact, the limit of possible decomposition is fixed very clearly at the hydrate containing $5{\cdot}5H_2O$. In the same way, the limits of the two branches of each of the curves representing the crystallisation of $H_2SO_4{\cdot}4H_2O$ and $H_2SO_4{\cdot}H_2O$, and that of the one branch of the H_2SO_4 curve, can be established from thermo-chemical considerations, and all these limits agree very well with the nature of the curves obtained experimentally.

1. *Mechanical Lowering.*—Considering the foreign molecules to be uniformly distributed throughout the solvent, and considering, also, for the sake of simplicity, that the molecules are stationary, the author argues that the solvent molecules will be entirely isolated from each other, and, therefore, will be prevented from combining to form the aggregates of which a solid is constituted, when there are 300 foreign molecules to every 100 molecules of the solvent. This value obtains only if we consider the molecules on a superficies, but the author argues on experimental as well as general grounds that crystallisation is entirely a surface action. The temperature below which a liquid will not solidify is −160°, according to Person (see *Trans.*, 1889, 32): hence 300 foreign molecules to the 100 will lower the freezing-point of water 160°, and one molecule will lower it by—

$$(160 \div 300 =)\ 0{\cdot}53°,$$

a constant closely approximating to that (0·63°) found by Raoult for various solvents freezing at about the same temperature as water. In the case of water, Raoult's work shows that the active molecule is not H_2O but $3H_2O$; the mechanical constant will, therefore, be $(0{\cdot}57 \times 3 =)\ 1{\cdot}6°$.

2. *Physical Lowering.*—If water be superfused to $t°$ below its normal freezing-point, and, then be made to crystallise, the heat evolved in its solidification diminishes regularly with the value for $t°$ from 1430 cal. per H_2O at 0° to *nil* at −160°; if $t°$ be −79°, or any lower temperature, the whole of the water will solidify, whereas for smaller values of t, the amount solidifying is given by—

$$\frac{t}{79},$$

and the heat evolved in this partial solidification will always be exactly sufficient to raise the resulting mixture of ice and water from $t°$ to 0°. If, however, we take a hydrate, say, $H_2SO_4{\cdot}13H_2O$, the freezing-point (water crystallising out) of which is −34°, the total water available for crystallisation is only $7{\cdot}5H_2O$, for no amount of cold would suffice to decompose the residual hydrate $H_2SO_4{\cdot}5{\cdot}5H_2O$; the amount of water which would crystallise would, therefore, be $\frac{34}{79}$ of $7{\cdot}5H_2O$, or $3{\cdot}2124H_2O$, and the heat evolved in its crystallisation is easily calculated, being 3615 cal. After the crystallisation a mixture of $3{\cdot}2124H_2O$ as ice, $(7{\cdot}5-3{\cdot}2124)H_2O$ as water and $H_2SO_4{\cdot}5{\cdot}5H_2O$ would remain, the total heat capacity of which is 223·5, and this mixture would be raised 16·17° by the 3615 cal. evolved, instead of 34° as would have been the case had there been nothing but the water present. The freezing-point, therefore, will have been lowered $(34°-16{\cdot}17°=)\ 17{\cdot}83°$ from this "physical" cause.

3. *Chemical Lowering.*—A definite hydrate such as

$H_2SO_4 13H_2O$ can only give up its water by decomposing into the next lower hydrate, $H_2SO_4 9H_2O$, in the instance taken: the heat absorbed in this change is given by the heat of dissolution curve (863 cal.), and will lower the temperature of a mixture with a heat capacity of 223·5 cal. by 3·5°.

The sum of these three lowerings gives −33·64° as the freezing-point, whereas −34·0° is the value obtained. The former is more strictly a calculated verification of the observed value than a calculated value; but it is in calculating the physical lowering only that the observed value is taken to start with, and the author finds that if a wrong value be taken for the freezing-point the "calculated" value does not agree with it, and that by a series of approximations we might ultimately obtain the true value starting with any temperature in the first instance. The following instances may be quoted:—

Hydrate.	Per cent H_2SO_4.	F. p. found.	F. p. calculated.
$H_2SO_4 130H_2O$	4·02	−1·59	−1·39
„ 60 „	8·59	−3·80	−3·44
„ 24 „	18·49	−11·83	−11·52
„ 13 „	29·53	−34·00	−33·64
„ 9 „	37·70	−72·63	−72·77

After the hydrate with $13H_2O$, the active water-molecule becomes simplified, attaining the formula H_2O before the hydrate with $9H_2O$ is reached. A similar simplification has been observed at about the same molecular composition in the case of mixtures of alcohol and water. Instead of calculating the freezing point, we may take the observed freezing-point and calculate the heat evolved in the chemical action, and, hence, the composition of the next lower hydrate formed in the reaction. The values given by the last three of the above-mentioned freezing-points are—

	Found. Per cent.	Calculated. Per cent.
Position of next hydrate	29·5	31·1
„ „	37·7	38·5
„ „	49·8	49·5

In the other two cases the chemical lowering is so small in comparison with the errors inherent in the calculations, that the calculated position of the next hydrate is valueless.

If no definite hydrates existed in solution, the chemical lowering would be absent; its absence would always increase the discrepancy between the observed and calculated values, and in the last three cases would destroy all semblance of agreement, the differences amounting to from 1·6° to 10·3°.

In the case of very weak solutions (0·36 and 0·37 per cent), the actual error between the observed and calculated values is less than 0·01°, but this is a relatively large quantity, and is probably due to errors in the experimental method adopted. A very striking confirmation of the composition of the hydrates at these points may, however, be obtained by comparing the figures representing the found and calculated values. Very definite proof is thus obtained that the author was wrong in supposing the existence of a hydrate with $510H_2O$ (1·0 per cent), but right as to the others.

The correctness of the calculated values affords proof not only of the position of the next hydrate, but also of their being a hydrate of the composition of the solution at which the freezing-point is taken. Points intermediate between definite hydrates may be correctly calculated on the supposition that the liquid consists of a mixture of next higher and next lower hydrate; whereas, if the calculation be based on the wrong supposition that the liquid consists of one definite hydrate, wrong values are obtained; thus:—

$H_2SO_4 16H_2O$ = 25·4 p. c.: the f. p. found was −23·0°; that calculated for a mixture of $H_2SO_4 24H_2O$ and $H_2SO_4 13H_2O$ is −22·36°; that calculated for a definite hydrate is −20·75°.

Very strong evidence of the existence of certain definite hydrates may be deduced from the limit assigned on thermo-chemical grounds ($H_2SO_4 5·5H_2O$) to the decomposition of the hydrates. Thus, taking the f. p. of the solution, $H_2SO_4 13H_2O$, we get −34° as the found value, and −33·64 as the value calculated with the above-mentioned limit; whereas, if the limit be taken to be the next hydrate above or below that with $5·5H_2O$, namely, those with 9 and $4H_2O$, we get −41·51 and −30·18 as the calculated values respectively; and, more important still, if we take that limit which would hold good on the physical theory of there being no definite hydrates in solution, which limit would be at about $H_2SO_4 7H_2O$, we get −37·11° instead of −34° as the calculated value.

The results obtained in calculating the lowering of the freezing-point of sulphuric acid by the addition of water, do not, from several causes, agree so well with the observed values as in the case of the water curve; but the differences are not great, and, though they prevent the correct calculation of the composition of the hydrates present, they are not sufficient to prevent our drawing from them further important confirmation of the general truth of the author's theory, and of concluding that the active molecules are, in this case, H_2SO_4 and H_2O respectively. The results mentioned are the following:—

	Per cent.	F. p. found.	F. p. calculated.
$36H_2SO_4H_2O$ ..	92·49	−3·05°	−1·89°
12 „ ..	98·49	−8·85	−7·38
6 „ ..	97·03	−18·60	−16·97
3 „ ..	94·23	−41·60	−38·61

These numbers representing degrees below the f. p. of the pure acid (10·35° C.).

In the case of the crystallisation of the monohydrate, the active molecule of sulphuric acid appears to be $12H_2SO_4$ throughout; while on the other branch of the curve where the f. p. is lowered by the addition of water, the "mechanical lowering" appears to be absent. This is probably due to the active molecule of water being very complex; if it were 12 times as big as it is when *it* is the crystallising substance (*i.e.*, the same proportion which obtains in the case of the sulphuric acid molecules), it would be $36H_2O$, and the lowering thereby produced would be practically negligible. The magnitude of the active molecules of the "foreign substance" in this case is probably due to the fact that the crystallising substance actually contains some of each of them, and therefore exerts less influence on them than would otherwise be the case. The fact that we have to determine the magnitude of the mechanical constant in the first instance from the curve does not detract much from the value of the deductions as to the calculated values; for one point is sufficient to give us the value of the constant, and we can then apply it in an indefinite number of other points. The instances given are—

Hydrate.	Per cent.	F. p. found.	F. p. calculated.	Next hydrate. Found. Per cent.	Next hydrate. Calculated. Per cent.
$H_2SO_4H_2O, \frac{1}{4}H_2SO_4$	86·40	−2·2	−2·36	89·10	88·46
„ ½ „	89·10	−9·8	−10·14	94·23	93·65
„ 2 „	94·23	(−60·7)	−63·19	—	—
„ ½ H_2O	82·36	−2·10	−2·13	78·41	78·45
„ ½ „	78·41	−15·41	−15·05	73·14	72·78

Of the 20 hydrates which the author has already announced as existing in the case of sulphuric acid, one has been definitely disproved by the present calculations; in the case of three others the evidence is insufficient to be termed proof; while proof of the most definite description is obtained in the case of the remaining. The hydrate $H_2SO_44H_2O$ is included, since the mere existence of the curve representing its crystallisation is ample proof of its existence, though there are no data existing in this case at present on which to found any calculations of the freezing-points.

DISCUSSION.

Professor RAMSAY said that it was impossible without careful study to offer any valuable criticism on so comprehensive a paper, opening up such new points of view. He drew attention to the fact that the supporters of Van't Hoff's theory of the existence of a substance dissolved in a liquid in a molecular state comparable with that of a gas by no means shut their eyes to the possibility, and in many cases the probability, of the existence of complex molecules, either of the solvent itself, or of compounds of the solvents with the dissolved substance. He also questioned the correctness of Person's data, on which it was assumed that the "solid-liquid critical point" was $-160°$, inasmuch as it is founded on insufficient data regarding the specific heats of solids and liquids at low temperatures. With reference to the sudden change in the molecular complexity of the water-molecule, assumed by Mr. Pickering to occur between the hydrate with $13H_2O$ and that with $9H_2O$, he suggested that a gradual disruption of the complex water-molecule would be more likely, and stated that from experiments of his own it appeared more probable that the water-molecule consists of $4H_2O$. The existence of complex molecules of sulphuric acid he regarded as supported by the fact of their being double sulphates of such formulæ as $NaH_7(SO_4)_4$.

Mr. PICKERING, in reply, said that it was quite true that Person's "absolute zero" of $-160°$ was more or less hypothetical. But it was founded on considerations precisely analogous to those on which the "absolute zero" for gases, $-273°$, was founded; and, just as the latter, though hypothetical also, yields correct results in all cases where true gases are concerned, so the former yields correct results in the case of liquids. He pointed out that the change of the acting water-molecule from $3H_2O$ to H_2O was not sudden, but was spread over a range 8 per cent in the strength of the solutions. There were no signs of the change beginning before the solutions attained the composition $H_2SO_413H_2O$. Finally, although, according to Raoult's work, the active molecule of water in this and in the majority of cases appeared to be $3H_2O$, there were other instances in which it attained the magnitude $4H_2O$.

100. "*The Constituents of Flax.*" By C. F. CROSS and E. J. BEVAN.

The authors describe the results of their examination of the cuticular constituents of the fibre, the only investigation of which hitherto published is that of F. Hodges (*Proc. R. Irish Acad.*, 1881, iii., 460).

On exhaustion with boiling alcohol, the fibre loses 3—4 per cent of its weight; as the solution cools it deposits a greenish white resin, which on hydrolysis with alcoholic soda yields a wax alcohol, identified as ceryl-alcohol. In addition to the alcohol an oily ketone-like substance was obtained. The residue appeared to be unresolved: on submitting it to drastic treatment with alkalies, two fatty acids were obtained, one of which, from its equivalent and melting-point, appears to be a cerotic acid. A considerable residue of unresolved products remained.

The green filtrate from the resin-wax yielded on distillation a green oily residue. From this a further quantity (10 per cent) of ceryl alcohol was isolated, and a much larger proportion of the oily ketone (15 per cent); the residue being a complex of ill-defined, inert compounds, yielding "ketones" on hydrolysis. These "ketones" have the characteristic odour of raw flax and flax goods, and from their property of emulsifying with water, no doubt exercise an important influence on the wet processes of fine spinning of flax.

The pectic group of constituents associated with the cellulose in the fibre proper was found to yield mucic acid on oxidation with nitric acid ($d = 1{\cdot}15$).

The isolation of a pure cellulose from flax is a difficult operation. The presence of unremoved cuticular constituents accounts for the statements of Godeffroy, that flax cellulose reduces silver nitrate when boiled with a neutral solution of the salt, pure flax cellulose resembling cotton cellulose in resisting the action of this agent. Flax cellulose oxidised with permanganate in alkaline solution yields, in addition to oxy-cellulose and oxalic acid, acid bodies, from which furfurol is obtained by acid hydrolysis.

101. "*Acetylcarbinol* (*Acetol*), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$." (Preliminary notice). By W. H. PERKIN, Jun., and J. BISHOP TINGLE, Ph.D.

This important substance, the first member of the series of ketone alcohols, has never been isolated, although its dilute aqueous solution has repeatedly been obtained. The authors have succeeded in preparing it in an anhydrous condition by the following method:—25 grms. of monochloracetone is slowly added from a dropping funnel to 200 c.c. of water containing an excess of freshly precipitated barium carbonate in suspension, the whole being vigorously boiled during the operation. As soon as the monochloracetone has dissolved, and the evolution of carbon dioxide has practically ceased, the liquid is filtered, and the resulting almost colourless solution is distilled. The distillate is now treated with chloracetone and barium carbonate and again distilled, the operation being repeated until 150 grms. of chloracetone have been treated. The resulting moderately concentrated solution of acetylcarbinol is saturated with potassium carbonate, and extracted at least 50 times with pure ether. The ethereal solution is thoroughly dried by means of ignited potassium carbonate, and is then slowly evaporated; a colourless oil remains, the greater part of which passed over on distillation between 140° and 150°. On refractionating, a considerable quantity was obtained boiling at 145—150°, which gave on analysis numbers agreeing with the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$, viz., $C = 48{\cdot}73$ and $H = 8{\cdot}33$, instead of $C = 48{\cdot}65$ and $H = 8{\cdot}11$.

Two vapour-density determinations by Hofmann's method in xylene-vapour gave $d = 35$ and 34, instead of 37.

Acetylcarbinol is a colourless oil, possessing a faint and peculiar odour, and a sweet but burning taste. It is miscible with water, and very readily reduces Fehling's solution in the cold.

When heated with excess of phenylhydrazine, it is converted into its osazone,—

$$\begin{matrix} CH_3{\cdot}C{:}N_2HC_6H_5 \\ | \\ CH{:}NH_2C_6H_5 \end{matrix},$$

which melts at 145°. This substance has already been prepared by Laubmann (*Annalen*, ccxlii., p. 244), and is identical with the compound obtained by Pechmann (*Ber.*, xx., 2543) from methylglyoxal and nitrosoacetone.

NOTICES OF BOOKS.

The Photographic Quarterly. Edited by C. W. HASTINGS. No. 1, October, 1889. London: Hazell, Watson, and Viney.

THIS new publication is full of good matter, and must be said to make an excellent beginning. Mr. C. H. Bothamley, F.C.S., contributes a sound paper on the chemistry of photography. In impressing upon the photographer the importance of an acquaintance with chemistry, the writer says:—"If his previous training

has been of a purely literary character, his want of familiarity with the scientific method will increase the difficulty." Here the truth is admitted, as Prof. Galloway insists that a purely literary training positively incapacitates the mind for the study of science. Whilst fully recognising that there is only one chemistry, he urges that "the same fundamental principles may be demonstrated and illustrated by very different sets of facts." He regrets that no elementary chemical text-book especially designed for the photographer has yet been written. In the same connection he remarks most truly that "adaptation to the antique syllabuses of examining boards has fossilised along a certain groove opinion as to what facts ought to be included in an elementary text-book on chemistry; and the resemblance between the very numerous chemical text-books now in existence is very like the resemblance between an equal number of pods of peas." Mr. Bothamley speaks almost as feelingly as if he had had to review a few dozen of such manuals.

In a paper on the "Influence of Photography on Art," Mr. A. M. Rossi looks forward into the dim future, when "another genius higher even than Daguerre will add colour to the photograph with the same truthfulness and vividness of nature."

The paper on "Photomicrography" is perhaps the most important of all. We perceive only one error. The writer, Mr. J. Hall-Edwards, L.R.C.P., says:—"When we remember that the number of species of plants and insects at present known has been estimated at 100,000." This is sadly below the mark. In all probability the number of one order of insects alone, the *Coleoptera*, does not fall far short of 100,000.

Mr. W. Jerome Harrison, F.G.S., contributes an interesting paper on the question, Was Photography discovered a Century ago?

Six candidates are mentioned: Matthew Bolton and F. Eginton, of Soho, about 1777; Thomas Wedgwood, of Etruria, and Humphry Davy, between 1794 and 1802; Lord Brougham in 1795; and Prof. Charles, of Paris, about 1780.

Lord Brougham's claim rests on an unpublishd part of a paper and on an experiment suggested, but not actually tried, and which, if tried, would have failed. Prof. Charles's candidature was rejected by Arago as not resting upon documentary evidence. The drawings produced "by mechanical means" at Scho were specimens of a method of engraving on copper, probably "*aquatint*." The part played by Wedgwood and Davy was much more important, and is reserved for discussion in the January issue, to which we look forward with much interest.

A Text-Book of Organic Chemistry. By A. Bernthsen, Ph.D., Director of the Scientific Department in the Chief Laboratory of the Baden Aniline and Soda Manufactory; formerly Professor of Chemistry in the University of Heidelberg. Translated by G. M'Gowan, Ph.D., Demonstrator in Chemistry, University College of North Wales, Bangor. London: Blackie and Son.

The author of this work has aimed at producing a small text-book, which, while not exceeding some thirty sheets in size, and of which the descriptive portion was condensed as much as possible, should yet be of a strictly scientific character; a book which, beginning with homologous series, should lay especial emphasis upon summarising the characteristics of each class of compounds, and, wherever possible, upon the inductive development of the theoretical relations existing between them.

In carrying out this idea Dr. Bernthsen has added another to the fairly numerous army of chemical text-books already in existence; a book in which it might be hard to detect any error, but the *raison d'être* of which is not beyond question.

We are glad to find that Dr. M'Gowan has not deemed it necessary to modify the book in accordance with the demands, open or implied, of any syllabus or examining body.

A few expressions occur which can scarcely be considered as good English. Thus, we are particularly sorry to see magenta spoken of as "fuchsin." The substance here named "alkali blue" is known by British manufacturers as "Nicholson blue." The translator also tells us of "compounds which *go into* the corresponding phenol dyes when boiled with water." "Pass into" would have been a more idiomatic expression.

CORRESPONDENCE.

THE IODINE ABSORPTION OF ESSENTIAL OILS.

To the Editor of the Chemical News.

Sir,—I exceedingly regret that I should have given the Editor of the *Chemist and Druggist*, and through him the readers of that publication, the slightest pretext for thinking that I have copied anything from his article on essential oils published in the issue of Oct. 19; nothing could possibly be further from my intention, and were it not for the innuendo cast upon my integrity by the note in last week's *Chemist and Druggist*, I should have considered it quite unnecessary to mention the fact that I had not seen the article of the 19th ult. until this morning.—I am, &c.,

R. A. Cripps, F.I.C.

Birmingham, Nov. 26, 1889.

WATER ANALYSIS.

To the Editor of the Chemical News.

Sir,—In an article on Water Analysis, by Mr. H. M. Vernon (Chemical News, vol. lx., p. 249), there occur several erroneous statements with reference to my process of water analysis, which I will thank you to allow me to correct.

1. I never evaporated water down, for combustion of the residue, in a *platinum* dish. The irregularities of the surface of such a dish would prevent, or render extremely difficult, the removal of the residue. The evaporation has always been performed in a glass dish.

2. The evaporation of a litre of water takes, at the most, eighteen hours, and not two days. It is the custom in my laboratory to begin the evaporation in the afternoon, and the dry residue is then ready for combustion at 10 o'clock on the following morning. That there is no access of dust, as alleged by Mr. Vernon, is, I think, proved by the fact that when the operations were removed from London to the much purer air of Reigate, no effect of the kind was perceptible.

3. I have never admitted, as alleged, that "nitrogenous organic impurities in the water" are decomposed and lost during evaporation; and, consequently, I have never "drawn up tables" showing the amount of such loss. I have drawn up tables showing the loss of ammonia during evaporation, but this loss has nothing whatever to do with organic matter; and the quantity of ammonia in potable waters is very rarely large enough to require any correction on this score. The tables are chiefly of use in the analysis of sewage and foul waters.

Had Mr. Vernon tried the process of evaporation *in vacuo* which he suggests, he would not have recommended it. I tested it thoroughly more than twenty years ago, and abandoned it as impracticable and affording no advantage.—I am, &c.,

E. Frankland.

The Yews, Reigate
Nov. 26, 1889.

IODINE VALUES OF OILS AND FATS.

To the Editor of the Chemical News.

Sir,—Seeing that the process known as the "iodine absorption" is mentioned in connection with the analysis of essential oils, may I be allowed to point out the importance of having a large excess of the reagent present? Neglect of this precaution renders results obtained by this test nearly, if not altogether valueless, and is not improbably the cause of many of the discrepancies between various observers.—I am, &c.,

J. A. Wilson.

Tottington, near Bury, Lancashire,
December 2, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 20, November 11, 1889.

The Incineration of Vegetable Matters.—G. Lechartier.—This paper will be inserted in full.

Simultaneous Solubility of Potassium and Sodium Chlorides.—A. Etard.—The author's experiments are summarised in the form of a diagram.

An Application of Thermo-Chemistry.—Alb. Colson.—It is tedious and difficult to demonstrate the identity or the dissimilarity of the alkaline functions in a polybasic alkaloid by the ordinary procedures of pure chemistry. In the case of nicotin, thermo-chemistry rapidly yields precious indications, which lead to the admission of dissymmetry in the constitution of this alkaloid.

No. 21, November 18, 1889.

Animal Heat and the Formation- and Combustion-Heats of Urea.—M. Berthelot and P. Petit.—In order to apply the author's rules and calculations, and to define accurately and in detail the production of animal heat, it is necessary to know the individual heat of formation and combustion of each of the compounds which intervene in alimentation, as well as that of each of the products eliminated by different channels.

Researches on the Application of the Measure of Rotatory Power to the Study of the Combinations Resulting from the Action of Malic Acid to Sodium Molybdate.—D. Gernez.—This paper is not adapted for useful abstraction.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., October, 1889.

Aniline Black and the Grawitz Processes.—This unfortunate controversy is still raging, and not merely experts, but courts of judicature, are giving contradictory decisions.

Falsifications of the Vegetable Oils of Commerce.—P. J. S. Girard.—The conclusion of this long and important monograph.

Manufacture of Ammonia.—Mr. Ludwig Mond.—From the *Journal of the Society of Chemical Industry.*

Improvements in the Manufacture of Sulphuric Acid.—F. Benker.—A new arrangement of towers to effect the more rapid condensation of the acid vapours. These are square or oblong towers of stoneware filled with a number of perforated plates of the same material. It is expected that these towers will shortly be substituted for the Gay-Lussac coke-towers.

Indian Ink.—B. Piffard.—From the Chemical News.

New Apparatus destined for the Analysis of Oils.—F. Jean.—This paper requires the four accompanying cuts.

The Great Chemical Industries at the Paris Exhibition of 1889.—P. Kienlen.—This paper treats exclusively of the manufacture of sulphuric acid, and concludes with the judicious wish that the use of an instrument so irrational as Baumé's may be abandoned.

A New Reagent for Cane-Sugar, Grape-Sugar, and Pyrogallic Acid.—Matthieu Plesy.—This reagent is a solution of lead paranitrate in melted ammonium nitrate, in which the pulverised lead nitrate is first dissolved. When nearly dissolved it is withdrawn from the fire and powdered litharge is added. The proportions are 45 parts ammonium nitrate, 34 parts lead nitrate $(NO_3)_2Pb$, and 21 parts lead oxide. This substance is cautiously melted by heat and a small quantity (0·005 grm.) of the substance in question is added, which gives a characteristic colouration, With glucose there is obtained a cherry-red colour. The substance is added before the complete fusion of the lead salt, the tube is withdrawn from the heat, and well shaken in an inclined position. For saccharose the lead salt is completely melted, the sugar is added, and the heating is continued until a *café au lait* colour appears. For pyrogallic acid sample is mixed with the solid salt, the whole is melted and heated until a chrome green appears.

Note on Turkey Red.—G. Saget.—Turkey red being a double alizarate of aluminium and calcium, it was interesting to know if the calcium could be replaced by another metal of the same atomicity, and what would be the tone of these new double salts. The use of any calcareous salt was carefully avoided. The alizarin was that for violets, and the metals were introduced into the dye-beck in the state of pure carbonates. Compared with a normal turkey red, the tones obtained were:—Barium, bluish red verging to crimson; strontium, red, slightly bluish; magnesium, bluish red-brown; manganese, yellowish red-brown; zinc, light garnet brown; nickel, light garnet violet; copper, dregs of violet; lead, light garnet red. The strontium red comes nearest to ordinary turkey red. All these double alizarates are equally fast.

Fermented Milk.—Ad. Tscheppe.—From the *Pharmaceutical Journal.*

Fatal Poisoning with Carbon Monoxide.—Prof. W. Mason.—From the Chemical News.

MEETINGS FOR THE WEEK.

Monday, Dec. 9th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 10th.—Institute of Civil Engineers, 8.
—— Royal Medical and Chirurgical, 8.30.
—— Photographic, 8.
Wednesday, 11th.—Society of Arts. "The Paris Exhibition," by H. Trueman Wood, M.A., Secretary to the Society.
—— Microscopical, 8.
—— Pharmaceutical, 8.
—— Sanitary Institute, 8. "The Disposal of Sewage," by W. Santo Crimp, Assoc.M.I.C.E.
Thursday, 12th.—Royal, 4.30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
Friday, 13th.—Astronomical, 8.
—— Quekett Club, 8.

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THE CHEMICAL NEWS.

Vol. LX. No. 1568.

CONSTITUTION OF BASIC SALTS AS EXEMPLIFIED BY A COMPARISON OF CERTAIN NITRATES AND PHOSPHATES.

By GEORGE WATSON, F.C.S.

Having had occasion some time ago to work at various methods of manufacturing pure phosphoric acid in large quantities, the common method of oxidation of phosphorus by hydric nitrate was tried amongst others, and during the experiments with it the analogies discussed below suggested themselves.

When phosphorus is heated with dilute hydric nitrate of sp. gr. about 1·200 it gradually disappears, evolving at the same time bubbles of a colourless gas which do not redden on admixture with air. This gas must, consequently, be either nitrous oxide or nitrogen. From some of my own experiments I am inclined to think that it consists of nitrogen in some cases, but as I have not yet proved this by direct experiment it may be assumed, for the basis of what follows, to be nitrous oxide. Then, inasmuch as burning phosphorus reduces this gas to nitrogen, we may imagine the phosphorus to be divided into two parts, one evolving nitrous oxide from the dilute nitric acid, the other burning in the nitrous oxide produced and forming nitrogen therefrom. Hence the operation may be viewed as a substitution of phosphorus for the nitrogen in nitric acid. Or it may be looked at in this way. As phosphorus burns in nitrous oxide, forming nitrogen, it should likewise burn in the more oxygenated compound, nitric oxide. This it is known to do; therefore it will burn in the highly oxygenated compound, gaseous hydric nitrate (HNO_3), displacing therefrom nitrogen. If, then, we imagine the substitution to be carried out with the latter substance, there will be formed the phosphorus analogue of HNO_3, viz., metaphosphoric acid. The substance symbolised HNO_3 may therefore be termed metanitric acid. If the substitution be performed in a mixed vapour of hydric nitrate and water, in the proportion $HNO_3 + H_2O$, there will be formed orthophosphoric acid. The hydrate HNO_3, H_2O, or H_3NO_4 is therefore analogous to orthophosphoric acid, and may be termed orthonitric acid. In the same manner, by substituting phosphorus for nitrogen in the vapour of $2HNO_3+H_2O$ we get $H_4P_2O_7$. Hence this hypothetical or unisolated hydrate is analogous to pyrophosphoric acid.

Taking these two series of acids, and forming metallic derivatives from them by substituting a divalent metal, we get as follows:—

Nitric Series.

HNO_3 —	$M''(NO_3)_2$	1.
$H_4N_2O_7$ —	$M''H_2N_2O_7$ or $M''(NO_3)_2H_2O$	2.
	$M''_2N_2O_7$ or $M''(NO_3)_2M''O$	3.
H_3NO_4 —	$M''HNO_4$ or $M''(NO_3)OH$	4.
	$M''_3(NO_4)_2$ or $M''(NO_3)_22M''O$	5.

Phosphoric Series.

HPO_3 —	$M''(PO_3)_2$	1.
$H_4P_2O_7$ —	$M''H_2P_2O_7$	2.
	$M''_2P_2O_7$	3.
H_3PO_4 —	$M''HPO_4$	4.
	$M''_3(PO_4)_2$	5.

Leaving on one side the phosphoric series of salts, and looking at the nitric series only, it is seen that, with the exception of Nos. 1 and 2, the other salts are basic nitrates of a divalent metal. Basic salts, corresponding to monobasic orthonitrates, have been prepared containing lead, zinc, cadmium, mercury (*ous* and *ic*) (*vide* Roscoe and Schorlemmer, "Treatise on Chem.," and H. Klings, *Ber.*, xvi., 997—999). Of normal pyronitrates, salts are said to have been isolated containing zinc and cadmium (H. L. Wells, *Amer. Chem. Jour.*, ix., 304—308), while a basic salt corresponding to triplumbic orthonitrate has also been prepared.

Dr. Perkin has recently adduced experimental evidence tending to prove the existence of orthonitric acid (*Proc. Chem. Soc.*, 1889, p. 130). Hence there is some reason for saying that all the basic nitrates which agree in formulæ with those required by the salts of this acid are not basic salts at all, but are in reality acid or normal orthonitrates, as the case may be; and the existence of orthonitric acid being in a measure proved, the probability of the existence of pyronitric acid is consequently increased. Whence, there also follows some reason for ceasing to view the salts of this acid as basic nitrates, and for looking at them as perfectly normal salts. And if this view be taken in the case of basic nitrates, may we not go a step further and view all basic salts as the normal or acid salts of hitherto unisolated hydrates of their respective acids? Professor Pickering has at various times promulgated the hypothesis that basic salts are strictly analogous to the hydrates of acids which exist in solution, and if it be agreed to view the various hydrates of a given acid as individual acids, differing from each other in the manner, although probably not in the degree, that the three acids of phosphorus differ from each other, then, I think, that the hypothesis becomes more significant. The term "basic salt" would then cease to have any special meaning, and all such salts could be ranged in the two groups of acid or normal salts, or, to speak more correctly, of partially and wholly substituted acids.

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DANGER FROM THE USE OF NATURAL GAS.

By F. MAXWELL LYTE, F.C.S., F.I.C.

It is worthy of consideration what will be the effect on the strata from which the natural gas which serves as the principal combustible in many parts of the United States is derived, as soon as it has all been used up and when it falls to the ordinary atmospheric pressure. This must assuredly take place sooner or later, and probably at no very distant period considering how rapidly the gas is being squandered. In the calculations below, the data on which they are founded are as follows:—

1. The average pressure at which the gas issues from the wells is said to be about 200 lbs. to the square inch = 28,000 lbs. to the square foot.
2. An acre contains 43,560 square feet.
3. A square mile contains 640 acres.

From these may be calculated the supporting pressure by which the overlying strata must at present be upheld from below.

Unless I am mistaken the gas would give a pressure which, for each square mile, would amount to no less than 358,436,571 tons, equivalent to the weight of a fair-sized mountain; so that on its ceasing to issue, proving thereby that the supporting pressure was withdrawn, the superincumbent strata would necessarily tend to give way. While the gas was there at so great a pressure there must have been an enormous pressure upwards, and when it disappeared this would probably be replaced by a still greater strain downwards.

The strata are already unable to support their own

Where M is less than 16 grms. in 100 grms. of water the green colour obtains, and calculation gives $r=4$; where M is greater than 20 (the change of colour takes place gradually between these two numbers), $r=12$. Hence, Rüdorff concludes that the green solution contains the salt $CuCl_24H_2O$, and the blue solution, $CuCl_212H_2O$.

Rüdorff next investigated the case of some double salts which for the quotient

$$\frac{T}{M}$$

gave decreasing values. Applying the formula (IV.) given above he found $r = -6$, and hence, concluded that these salts, though in the solid form combined with six molecules of water, dissolve in water as anhydrous salts, their water of crystallisation being added to the solvent water.

In 1871 and 1872, De Coppet published, in the *Annales de Chimie et de Physique*, lengthy criticisms on Rüdorff's paper, and compared his results with those arrived at by Despretz in his paper on the points of maximum density.

De Coppet examined a number of salts of the alkalies and alkaline earths, and concluded that in some cases the salt is partially decomposed in solution — but he added to the coincidences worked out by Rüdorff, the following important fact :—

In the case of KCl, KBr, and KI, *if the quotient*

$$\frac{T}{M}$$

be multiplied by the molecular weight of the salt in question, the product is approximately the same in the three cases :—

For KCl	.. .. ..	0·455 ×	74·6	= 33·9
„ KBr	.. .. ..	0·292 ×	119	= 34·8
„ KI	.. .. ..	0·212 ×	166	= 35·2

In other words :—

An equal number of molecules of chloride, bromide, and iodide lowers the freezing-point approximately the same number of degrees.

This quantity,

$$\frac{T}{M} \times A,$$

De Coppet calls the *atomic depression* of the freezing-point.

$$\frac{T}{M}$$

he calls the *coefficient of depression*.

(To be continued).

THE INCINERATION OF VEGETABLE MATTER.

By G. LECHARTIER.

The incineration of vegetable matter is a delicate operation when we wish to avoid any loss of the mineral matter by mechanical dispersion or by volatilisation. Under various circumstances special precautions have been observed. M, Schlœsing first effects the slow carbonisation of the substance in an atmosphere of carbonic acid, and then burns the carbon by means of oxygen. M. Berthelot conducts the combustion in a current of oxygen, passing the products through a column of sodium carbonate heated to dull redness.

These precautions seem to regard losses as possible. The author therefore thinks it useful to inquire if losses may be avoided in incinerations in the open air, and to determine what is their amount in cases where they necessarily occur. This question is interesting, not merely for future investigations, but also concerning former researches emanating from distinguished *savants* whose name carries authority.

In every incineration we may distinguish two principal facts :—

1. Carbonisation of the vegetable matter, with disengagement of watery vapour, tar, gaseous hydrocarbons, and various volatile products.

2. Partial combustion of the vapours and complete combustion of the carbon, which still forms part of every fragment of the matter after the complete disappearance of everything volatile. During this last part of the process the phosphates are exposed to more or less elevated temperatures in contact with carbon and in presence of silica.

The author has studied the two phases of the process separately. He has incinerated grains of wheat and buckwheat, entire plants, wheat cut at the time of flowering, tubers of Jerusalem artichoke, and the straw of buckwheat. Forty to fifty grms. of the substance were operated upon at once.

1. *Carbonisation of the Vegetable Matter.*—This process was effected in a small platinum retort, the head of which was adjusted to the body by simple rubbing. The neck of the retort was connected by a cork to a refrigerated receiver, the second tubulure of which communicates with a bulb-tube containing strong nitric acid. A regular aspiration is kept up in the apparatus by means of a water-sprengel to prevent any excess of pressure and loss of vapours at the point of junction of the head and body. The retort is heated by means of a strong Bunsen burner, the flame of which is gradually raised so as to bring the matter gradually to redness. At the end of the operation a temperature is reached higher than is required for incinerations in the open air. The liquids condensed are evaporated with the nitric acid after the addition of pure lime. The product of the evaporation is ignited to destroy the tar. After re-dissolving in water and nitric acid he pours into half the liquid an acid solution of ammonium molybdate, and into the other half a solution of barium nitrate.

The liquid contained in the bulb tube is submitted to an identical operation.

In every case a precipitate of barium sulphate is obtained. Most frequently there is no formation of a yellow precipitate of ammonium phosphomolybdate. In the cases when some trace of a precipitate is formed it is redissolved in ammonia and magnesium nitrate is added, but the ammonium-magnesium phosphate is not precipitated on taking the results of a single operation.

The molybdic precipitates obtained in six successive experiments were collected when the ammonium-magnesium phosphate became appreciable; it yielded 0·001 grm. pyrophosphate for a quantity of matter corresponding to 120 grms.

The precipitates of barium sulphate corresponded to weights of sulphur ranging from 11 to 54 m.grms. in 400 grms. of the vegetable matter.

These experiments were varied as regards the phosphorus. In a second series of experiments the platinum tube was placed in connection with a tube containing a column of sodium carbonate followed by a column of quicklime. The sodium carbonate was heated to incipient redness and the lime to bright redness. The tube was followed by a condenser and this again by a tube containing nitric acid. In the carbonisation of 80 grms. of wheat, 1 m.grm. of phosphoric acid was extracted from the matter condensed in various parts of the apparatus, but it is not certain that nothing was carried away mechanically.

2. *Combustion of Carbon.*—Grains of wheat previously carbonised were heated in a current of oxygen, and the gases were passed over a column of lime raised to bright redness. The lime when dissolved did not yield a trace of phosphoric acid. The operation was performed on 25 grms. of wheat.

3. In *mixed experiments*, where the carbonisation was followed by incineration, more or less prolonged, no phosphoric acid was found in the volatile matters,

whether they were condensed in a receiver or passed over sodium carbonate heated to dull redness.

4. Lastly, it seemed useful to determine the phosphoric acid in one and the same vegetable:—(1) On incinerating in oxygen in a tube containing a column of sodium carbonate; (2) on incinerating in a platinum capsule in the air; (3) on incinerating after having moistened with milk of pure lime at 5 per cent and drying; (4) using a solution of calcium nitrate containing an excess of lime. This solution does good service in incinerating organic manures; but with grain it may occasion deflagration with loss of matter.

The proportion of phosphoric acid found in 100 parts of wheat (grain only) was, on incineration in oxygen, 0·770; in the open air, without addition, 0·767; in presence of lime, 0·770; and in presence of sodium nitrate (? calcium nitrate), 0·780.

The slight differences found in these results are within the possible limits of experimental error and of the variations of composition which may occur in two samples of the same vegetable.

In fine, in the carbonisation and incineration of a vegetable there is a notable loss of sulphur volatilised in different combinations, a part of which may be condensed in a liquid state. Special precautions are necessary for determining the sulphur.

Under the same conditions, if all carrying off solid matter by the escaping vapours and gases is prevented there is no appreciable loss of phosphorus.

The incinerations in the air were effected as follows:—The platinum capsule containing the substance is placed on a piece of tile which is heated in a gas-furnace. The capsule is covered with an inverted gas-funnel, which is kept slightly raised above the capsule. The heat is applied gradually, beginning with the smallest possible flame, so as to produce a slow escape of vapours and gas. When this escape ceases the bottom of the capsule is raised to nascent redness for a few moments, so as to complete the decomposition of the vegetable matter. The carbon is washed with hot water, decanting the liquid over a paper filter; three or four washings with a small quantity of water are sufficient. The filter, with its contents, is introduced into the capsule, dried, and heated to dull redness, when the incineration is rapidly effected. The liquid from washing the carbon is added to the ash, evaporated to dryness, and weighed; or the residue is treated with nitric acid.

If this treatment with nitric acid shows small particles of carbon they are filtered off and incinerated, adding their ash to the rest of the matter. This carbon still contains phosphoric acid, notwithstanding the acid washings.

For determining the phosphoric acid it is advantageous to mix the substance intimately with milk of lime sufficient to moisten all its parts. The mixture is dried and ignited. —*Comptes Rendus* (Vol. cix., p. 727).

ISOMERIC NAPHTHALENE DERIVATIVES.*

The study of naphthalene derivatives has been prosecuted in the reporter's laboratory during the past year with far greater success than could have been anticipated, chiefly owing to the untiring energy and skill of Mr. W. P. Wynne; valuable assistance having also been rendered by several students. The results are, it is believed, of considerable importance from a theoretical point of view, not merely in relation to naphthalene derivatives, but in connection with the general problem of the nature of the changes involved in the production of isomeric compounds.

Constitution of the Isomeric Dichloronaphthalenes.—A list of the twelve reputed dichloronaphthalenes was given in the last Report, and their constitution was provisionally discussed. The results since obtained render it possible to finally assign the proper formulæ to the several modifications, the method adopted affording almost, if not quite, as absolute a determination of their constitution as that employed by Körner in the case of the dibromobenzenes: an account thereof is given in the *Proceedings of the Chemical Society*, 1888, pp. 104—107; 1889, pp. 34—37; pp. 48—54. The conclusions arrived at by Erdmann and Kirchhoff are confirmed; as the synthetic method which these chemists had adopted was one which did not exclude the possibility of the occurrence of isomeric change, objection was taken to their proof in the last Report, but it is now clear that they had correctly interpreted their results.

The so-called α-dichloronaphthalene, m. p. 38°, obtained by the action of alcoholic potash on naphthalene tetrachloride, has been proved to be a mixture of 1:4 (β) dichloronaphthalene, m. p. 68°, and 1:3 (θ) dichloronaphthalene (m. p. 61°) (*cf. Chem. Soc. Proceedings*, 1888, 106). It has previously been pointed out that the so-called κ-dichloronaphthalene of Claus has no claim to recognition, and that it is doubtful whether the ε dichloronaphthalene described as melting at 120° was a pure substance; consequently at present but nine of the ten possible dichloronaphthalenes are to be regarded as beyond doubt existent; their constitution is as follows:—

		M. p.	Position of radicles.
αα.	Modifications:—		
	β. Dichloronaphthalene..	68°	1:4
	ζ. „ ..	83°	1:1′
	γ. „ ..	107°	1:4′
ββ.	Modifications:—		
	δ. „	114°	2:2′
	ε. „	135°	2:3′
αβ.	Modifications:—		
	— „	34°	1:2
	θ. „	61° (about)	1:3
	θ′. „	63° „	1:2′
	η. „	48°	1:3′

The Alpha law. Spontaneous occurrence of Isomeric Change on Sulphonation.—In previous reports attention has frequently been directed to the circumstance that, as a rule, *alpha*-derivatives are formed, and that *beta*-derivatives are only obtained either when a group is present in an alpha position, which determines the entry of the new group into the contiguous beta position, or owing to the occurrence of secondary change; it has, in fact, been argued that an isolated beta position is never directly attacked. Further evidence, tending to strengthen this conclusion, has recently been obtained. When either β-chloro- or β-bromonaphthalene is sulphonated, the chief product is the 2:1′ α-acid; and a relatively very small amount of the isomeric 2:3′ β-acid is also obtained, and it was suggested that this was formed by spontaneous isomeric change from the 2:1′ acid, as it was found possible to convert the α- into the β-acid by heating. β-Iodonaphthalene, in like manner, was found to yield two sulpho-acids, but it was pointed out in the second of these reports that the melting point of the sulphochloride of the acid found in small quantity was remarkably low. Recent experiments of Mr. Houlding (*cf. Chem. Soc. Proc.*, 1889, 74) have served to show that the minor product is not the 2:3′ derivative. Subsequently, Mr. Wynne and I have found (*ibid.*, 1889, 119) that the chief product of sulphonation in the case of β-iodonaphthalene corresponds with the chief product afforded by β-chloro- and β-bromonaphthalene, and that the minor product obtained from β-iodonaphthalene is the second heteronucleal 2:4′

* Fourth Report of the Committee, consisting of Professors Tilden and Armstrong (Secretary), appointed for the purpose of investigating Isomeric Naphthalene Derivatives. (Drawn up by Professor Armstrong). Read at the Newcastle-upon-Tyne Meeting of the British Association, 1889.

alpha-sulphonic acid: so that whereas only one alpha-acid is obtained on sulphonating β chloro- and β-bromo-naphthalene, β-iodonaphthalene yields the two possible heteronucleal alpha-acids. Both β-iodo α-sulphonic acids, however, are found to yield the same 2 : 3′ β-sulphonic acid when heated at about 150°. It is therefore not improbable that on sulphonating the chloro- and bromo-compounds, two *alpha* acids are initially formed, and that one of these forthwith undergoes spontaneous isomeric change into the 2 : 3′ acid.

The results obtained in the case of the dichloronaphthalenes tend to support this view. Thus, 1 : 3 (θ) dichloronaphthalene affords but a single sulphonic acid; this product is identical with that prepared by Widman from naphthalene α-sulphonic acid, and is in all probability the 1 : 3 : 4′ acid.

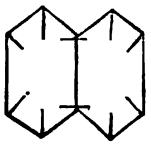
1 : 2 dichloronaphthalene, however, yields two isomeric acids, the chief product (about ⅔) being the 1 : 2 : 4′ (α) acid, the subsidiary product, the 1 : 2 : 3′ (β) acid; as the latter is almost the sole product if the original product of sulphonation be heated at 150°—160° during several hours, it is probable that the β-acid in the original product is formed by spontaneous isomeric change at the moment of sulphonation.

1 : 4 (β) dichloronaphthalene, however, yields as sole product the 1 : 4 : 2′ (β) sulphonic acid, and it would appear that isomeric change takes place in this case spontaneously and with exceptional facility and completeness.

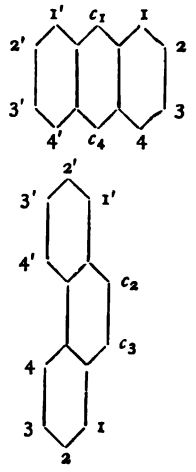
1 : 4′ (γ) dichloronaphthalene yields as chief product (about four-fifths), the 1 : 4′ : 2′ beta-sulphonic acid (m. p. of sulphochloride 139°—140°), together with what appears to be the isomeric 1 : 4′ : 3′ beta-acid (m. p. of sulphochloride 98°—100°); in this case it is possible that an alpha-acid is first formed, which at once changes, but more probably the two alpha positions are "protected" by the two alpha-chlorine atoms, the 1 : 4′ : 3′ beta-acid being first formed, and at once partly converted by spontaneous isomeric change into the more stable 1 : 4′ : 2′ acid. It is obvious that much important information is to be obtained by further study of this subject.

Azo-Dye Stuffs Derived from Naphthalene.—In the second of these reports it was argued that the azo-dye stuffs from betanaphthol were all 1 : 2 α-β-derivatives, and, as a matter of course, the argument would apply equally to betanaphthylamine. Experiments were commenced with the object of obtaining the data required to verify this theory, but their continuance became unnecessary in consequence of the publication of a valuable paper by Dr. O. N. Witt (*Berichte*, 1888, 34—68), in which it is demonstrated that the azo-colours from the four isomeric betanaphthylaminesulphonic acids and a number of others are all 1 : 2 derivatives. In pointing out (*cf. second* report), that the formation of the azo-colour involves an isomeric change which apparently can take place only in the one direction, and that on this account it is impossible to effect the introduction of the azo-group into any other position than that contiguous to the OH or NH_2 group, no special note was taken of the peculiar constitution of the colouring matters themselves; the further study of this question, however, has led me to the conclusion that even if the transference could be effected in any other way, azo colours would only result provided that "quinonoid" compounds were formed; at present this is only known to obtain in the case of the 1 : 2 and 1 : 4 compounds (*cf. Chemical Society Proceedings*, 1888, p. 27).

The Symbol of Naphthalene.—There appears to be a tendency on the part of some recent investigators of naphthalene derivatives to consider that the naphthalene molecule is dissymmetric. Without discussing this question in detail I would express my conviction that this is not the case, and that the behaviour of naphthalene, and especially its characteristic tendency to form alpha-derivatives, may be satisfactorily expressed by means of a symbol similar to that which I have suggested for benzene (*Phil. Mag.*, Feb. 1888), viz.:—



Notation of Naphthalene Derivatives.—Throughout these reports, &c., the system of notation introduced many years ago by the Chemical Society and in "Watts's Dictionary of Chemistry" has always been made use of, and its general adoption was advocated in a recent paper by Mr. Wynne and myself (*cf. Chem. Soc. Proceedings*, 1889, p. 54). It consists in numbering the positions in the one nucleus 1, 2, 3, 4, and the corresponding positions in the second nucleus 1′, 2′, 3′, 4′. The practice of numbering the positions 1 to 8 appears less desirable and rational in view of the fact that naphthalene consists of two like nuclei, and of the importance of at once being able to recognise which are corresponding positions. In a recent conference at Paris it was, however, resolved to recommend the system of numbering the positions 1 to 8, but this decision appears to have been arrived at without any sufficient discussion of the question or pains being taken to consult those who have the right to express an opinion. The desirability of numbering corresponding positions similarly in all multinuclear compounds cannot be denied, and it is very easily carried into practice; thus in the case of phenanthrene the positions in the one *lateral* nucleus are 1, 2, 3, 4, in the other 1′, 2′, 3′, 4′, and in the *central* nucleus c_2, c_3; in the case of anthracene those in the central nucleus are c_1, c_4, those in the one *lateral* nucleus 1, 2, 3, 4, those in the other 1′, 2′, 3′, 4′. Thus:—



Anthraquinone is a 1 : 4 *centri*-di-derivative, phenanthraquinone a 2 : 3 *centri*-di-derivative.

Employment of Electric Conductivity for the Study of the Displacements and Distributions of Acids of Complex Functions.—Daniel Berthelot.—Aspartic acid is one of those bodies which unite an acid and an alkaline function. The author has undertaken to study the equilibria produced in the presence of this acid in dilute saline solutions. These equilibria depend on the presence of the antagonistic acids, which, on the one hand, may seize upon the whole or a part of the mineral base, and, on the other, may combine with the aspartic acid itself. The conductivities were measured by means of Lippmann's capillary electrometer.—*Comptes Rendus*, Vol. cix., No. 22.

THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

Continued from p. 275).

Outside, one might say even within, the laboratory the properties of the metalloid silicon, or silicium, are but little known. No fuller details can be found than in that part of Dr. Percy's work, "Metallurgy," relating to silicon, where all the methods for its production on a laboratory scale are given.

It is ordinarily described as a non-metal, very hard, dark brown in colour, a non-conductor of electricity, lustrous, not readily oxidised, and soluble in all ordinary acids with the exception of hydrofluoric. It is said to resemble carbon in its general properties. Others add that it exists, like carbon, in a graphitic, amorphous, and combined or adamantine form; but this is still to be determined.

Mr. Henry J. Williams, St. Louis, Missouri (U.S.A.), this year presented a paper to the American Institute of Mining Engineers on "The Determination of Silicon in Ferro-silicons: its Occurrence in Aluminium as Graphitoidal Silicon, and a Study of its Reactions with Alkaline Carbonates." As the latest investigation of this kind, it may be well to refer to the experiments. Mr. Williams's method of determining the metalloid was by means of fusion with sodium carbonate, the idea being to dissolve it as soluble sodium silicate, and leave the iron in a very spongy and finally divided condition so as to be readily attacked by acids. He noticed some curious facts during fusion. As soon as the sodium carbonate was thoroughly melted and the heat reached its maximum, the reaction became very violent, bubbles of gas (carbonic acid) rising to the surface and bursting into flame. This had been noticed before by another observer making experiments of similar nature with graphitic pig-iron. Mr. Williams was, however, somewhat puzzled, as the ferro-silicon with which he was experimenting was high in silicon and comparatively very low in carbon; yet it gave the same result. To ascertain why silicon acts exactly like carbon during the reduction, he endeavoured to obtain an iron entirely free from foreign elements, particularly carbon, but containing high silicon, but was unsuccessful. He found the desired condition realised in the aluminium of trade, most of which, in spite of its name, he states, contains not less than three per cent or four per cent of silicon, but of course no carbon. He found that a large part of the silicon in such aluminium seemed invariably present as an allotropic modification of that metalloid, crystallising in fine glistening black plates resembling some forms of graphite, and considered that this was evidently the graphitoidal form of silicon which Deville has mentioned in connection with aluminium, but which has not yet been isolated or found to exist in iron. Dr. Percy mentioned at length the same fact, and describes the material as resembling graphite from iron smelting furnaces, and as being hard enough to scratch glass, with a specific gravity of 2·49. As regards, however, the form silicon may take in cast-iron or steel, Mr. Keep considers that whether it exists in a state corresponding to graphitic carbon, and mechanically mixed with the remaining mass, is still a question in dispute. Mr. Holgate, of Darwen, also, in the paper before referred to, after making many analyses, says he has never found any evidence as to the existence of graphitic silicon in such alloys, though he has noticed some slight difference in the behaviour of silicon when dissolved in acids. Mr. Turner, in his paper some two years ago, after carefully investigating this point, both by means of experiments of his own and those of Sir Frederick Abel, Mr. Snelus, and others, says that it may at any rate be considered, in a vast majority of cases at least, silicon has only one form. Finally, therefore, the practical metallurgist has at present, apparently, no means of readily determining this point, although he may have reason to think that silicon does vary its form in either cast-iron or steel.

In metallurgical literature but little information is to be found as to the effect of silicon upon iron. Mr. Howe, in his excellent work on "The Metallurgy of Steel," gives an excellent *résumé* of what has appeared. Some fourteen years ago in America good results were promised by a process which was to use "codorus or silicon ore," as it was termed. This was to dephosphorise or neutralise the phosphorus in the metal under treatment. Only a few years back the writer had reason to investigate this matter in America, but found that this so-called puddled silicon iron or silicon steel contained no silicon. The whole matter was well summarised by the well-known metallurgist, Holley, of America, who said, or rather sang of it,—

> There was an old man of Codorus
> Who said he took out the phosphorus,
> So the iron he puddled and with chemicals muddled,
> But the puddling took out the phosphorus.

Referring now to the consideration of silicon alloyed with the metal iron, the common belief has been that steel which has to be used in its forged state should contain practically none or as small an amount as possible. Any quantity exceeding 0·10 per cent, or up to 0·20 per cent at most, has been considered to be highly injurious. "Give a dog a bad name" is well illustrated in the present case, as will be seen from the results and tests given. At any rate it may be safely said that silicon has been blamed in a somewhat hasty manner. This blame may be well deserved in alloys of carbon, silicon, and iron, as such alloys as regards ductility have, no doubt, proved unreliable and of little value; but the blame was put at the door of silicon, whereas it is now proved that silicon alloyed with iron, provided carbon is absent, or only present in small amounts, gives good tests as to toughness and malleability. It will be seen that 1½ or even 2 per cent may be present and yet the material possess 25 to 30 per cent elongation; whereas the same percentage of carbon alloyed with iron would give a product barely malleable, and one possessing practically no properties of elongation under tensile stress. Whilst, therefore, the common belief that alloys of carbon, silicon, and iron are brittle, or even dangerous, is quite correct, the cause is not due to silicon only, but to the combination of silicon with carbon and iron—a case parallel, to some extent, to that pointed out by the well-known Terre Noire Company's experiments, where it was proved that phosphorus may be present in iron provided the carbon is low and the manganese high; a fact—that is, as regards phosphorus—still more prominent in wrought irons. As also pointed out by Mr. Howe, "Silica is often mistaken for silicon: who knows how far it is responsible for this metalloid's bad name?" This was actually noticed by Mr. Turner in test bars of steel containing comparatively low percentages of silicon—that is, under 0·5 per cent—much of the silicon present being in the oxidised condition.

Also, according to M. Gautier, there is a difference between steel made with silicon only and that with silicon and manganese, *i.e.*, between a product made by adding ferro-silicon (carbon, silicon, and iron alloy) and that with silicon-spiegel (carbon, silicon, manganese, and iron alloy); and he mentions the following interesting experiment by his then colleague, M. Pourcel.

In a porcelain tube were placed two receptacles, one holding steel made by adding ferro-silicon only, and the other steel by an alloy of silicon-spiegel. A current of chlorine was passed until all the iron was removed in the state of chloride. It was then seen that in the first receptacle there remained a network of silicate of iron preserving the original formation of the piece, whilst steel

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B, Newcastle Meeting.

by silicon and manganese alloy left no residuum. Also, that such steel with no manganese was red-short, lacked fluidity, and possessed other defects. The writer has, however, not noticed such difference in the material now described, which in its molten state pours well, the ingots forging easily, and up to two per cent silicon the ductility in the testing-machine being very good.

However, as suggested by Mr. Howe, possibly silicon does enter into different combinations in steel, some promoting, some impairing ductility and malleability. In favour of this is the fact that so many well-known scientists and metallurgists have utterly condemned in forged steel the employment of silicon, even if present in small amounts. Such strong opinions would not be expressed without good grounds, and a reasonable explanation for the apparent discrepancy noticed by different observers seems to some extent to be in the direction named. At any rate the samples described in this paper, and containing up to two per cent, present a remarkable ductility and toughness both in the bending and tensile specimens.

The writer wishes it to be understood that he does not claim that silicon should take the place of carbon. Smaller quantities of carbon produce the requisite hardness and different tempers required in the industrial application of steel, and in fact silicon alone does not produce a steel that will harden by water-quenching, thus in this respect resembling manganese steel. Still it is a somewhat remarkable fact that a steel (specimen C) containing 1·60 per cent of a metalloid ordinarily so much distrusted stretched 35·10 per cent (on 2″), with 54·52 per cent reduction in area, and a test bar from the same material tested by Professor Kennedy gave 24·30 per cent (on 10″), with 58·30 per cent reduction in area. Also, had not the specimen D, tested by Professor Kennedy, broken in the threads (the diameter of the bar over the threads being only 0·93 against 0·898 of the tested part of the bar: too small a difference with hard steel in the holding part) no doubt his test would have confirmed the writer's, that a material with even 2·13 per cent of silicon will elongate 36·50 per cent on 2″ (equivalent to about 27 per cent on 10″), with 59·96 per cent reduction in area. So that whilst it may not be advisable to use silicon as a hardener in making steel, it is important to have it proved that the brittleness noticed in ordinary so-called silicon steel is due rather to the combined presence of the two hardeners, silicon and carbon. It may be here mentioned that the ductility noticed cannot be attributed to manganese, which was only present in small quantities, about 0·20 to 0·30 per cent.

The material employed in these experiments was made by melting in crucibles good wrought-iron scrap, low in sulphur and phosphorus, to which was added in varying and increasing quantities a rich ferro-silicon containing 20 per cent of silicon. The ingots, 2½ inches square, were reduced by forging in the ordinary method to 1¾-inch square billets, then rolled down to bars 1¼-inch diameter.

The effect of silicon upon iron is as follows; (1) in its forged condition; (2) in its cast condition:—

1. *Forged Condition*.—The forge reports that the material A (0·24 per cent Si) did not forge well, cracking somewhat whilst being hammered, but all the other samples, B to H (0·79 per cent to 5·53 per cent Si), when forged at a fair yellow heat required no special care; thus clearly showing that silicon even up to as high as about 6 per cent does not destroy the malleability of the metal iron. Upon, however, exceeding this percentage the material is red-short, crumbles at a low heat, and, notwithstanding the low percentage of carbon present (0·25 per cent), becomes really a species of cast-iron. It should also be here mentioned that if the carbon had been higher the point at which malleability ceases would have been with a much lower percentage of silicon.

Nor is such red-shortness removed by the addition of manganese.

It may also be here mentioned that no return of strength takes place by a further addition of silicon, as is so specially characteristic of manganese steel. Any further addition merely increases its resemblance to siliceous cast-iron. Nor do gradually increasing percentages, as is the case with manganese steel, destroy the magnetic properties of the alloy; a 7 per cent material seems quite as susceptible as ordinary iron drillings.

Apparently silicon up to 1¼ or 1¾ per cent added to iron, although increasing the limit of elasticity and raising the tensile strength, does not impair ductility, but after this the further increase of tensile strength noticed is only obtained with a serious loss of ductility. Apparently there is no sharp line of demarcation. After passing 1¼ per cent further slight increases cause great changes in the characteristics of the material. In this respect, therefore, its action rather resembles that of carbon in contradistinction to the action of manganese, of which much larger amounts are required to effect similar changes.

The fractures from the tensile test-bars up to "D" specimen (2·18 per cent Si) are silky, after this completely and coarsely crystalline. As in the specimens in the cast state, neither annealing nor water-quenching seem to have any effect on the structure.

The annealed flat bending pieces, ½ inch wide by ¼ inch thick, gave good results, specimens A, B, C, and D (0·24 per cent to 2·18 per cent Si) bending double cold without fracture, more like dead soft steel, and, after being bent double, the pieces were flattened close together cold without showing signs of fracture. Specimen E (2·67 per cent Si) also bent double cold, but broke in the radius with the least blow. F (3·46 per cent Si) was much stiffer, and bent only to a right angle. G and H (4·49 per cent and 5·53 per cent) would not bend at all, and were exceedingly brittle. These bending tests were confirmed by Mr. Turner's experiments with bars of the same size; up to D specimen the samples bent to an angle of 180° with ¼ inch radius.

Pieces from the bars used for bending tests were also tested for weldability, but entirely without success. The writer's experience has always been that silicon is quite fatal to welding, notwithstanding that the contrary might be expected from the fact that silica is of such material assistance in welding wrought-iron.

As regards water-quenching or hardening, samples A, B, C, and D (0·24 per cent to 2·18 per cent Si) were unaffected by even the highest heat. Even if plunged at welding-heat into water made specially cold no hardening beyond a surface stiffening took place, nor did their toughness seem impaired by this treatment. Specimen E (2·67 per cent Si) was heated to an ordinary yellow heat and plunged into cold water at about 70° F. This piece was much stiffened, but only broke on being bent double. Another piece of the same material, heated to a welding heat and plunged into water at about 52°, also proved very stiff, and only broke when bent double; F (3·46 per cent Si): this sample was only stiffened by being water-quenched at a welding heat. It was just as brittle as before, and had not hardened, being easily touched by a file. In this respect, therefore, *i.e.*, as to being toughened by water-quenching, this material differs from manganese steel. The heating did not cause much alteration in fracture, the crystallisation being still open and coarse. H (5·53 per cent) was quenched both at ordinary heat and at a welding-heat, and although the surface was skin-hardened, upon being fractured it was easily filed. These tests, therefore, clearly prove that silicon does not confer the same property as carbon does upon iron, *i.e.*, of becoming hardened when dipped hot into a cooling medium. It should also be here stated that the whole of the samples were subjected to high heats, even to a welding temperature, without falling to pieces; in fact, as regards this point, they behaved more like mild steel; apparently proving that silicon itself does not cause iron to become red-short.

That silicon steel has a certain kind or degree of softness or lack of body compared with carbon-steel is especially brought out in the compression tests, where sample E, although apparently very hard and brittle (high in the scale of Turner's hardness tests, viz., 33), crushed up 38 per cent of its length under a compression load of 100 tons per square inch. A correspondingly hard temper of carbon or tungsten steel would not shorten more than 20 per cent, or, if hardened, would remain unaltered. A very mild steel, containing not more than 0·20 per cent of carbon, would not shorten much more than this sample, containing over 2½ per cent of silicon. At any rate, therefore, silicon is not so powerful a hardener of iron as is carbon. Mr. T. Turner has tested this material in his sclerometer, or hardness-testing machine, the results of which are given under this head in Table I.

In order to test this steel in the shape of wire, samples E (2·67 per cent Si) and G (4·49 per cent Si) were reduced to rods, and Messrs. Shipman and Co., of Sheffield, kindly undertook to draw them into wire. The G material, though readily rolled into rods, would not, however, draw, nor did annealing soften or give it the requisite ductility. In the rod state the tensile strength was 19 tons per square inch, with 12 torsions in 8 inches. Crucible carbon steel would stand about the same test, and Swedish Bessemer with high carbon slightly higher in torsion, but lower in tensile strength.

The material, E, was readily drawn to No. 20 B.W.G., standing 180 lbs. tensile strength (64 tons per square inch), with 157 torsions in 8 inches. Annealing lowered the tensile strength to 120 lbs. (about 48 tons per square inch), and slightly increased the torsions to 169 in 8 inches. The wire-makers endeavoured to harden both G rods and E wire both in oil and water, but without success.

Professor Barrett, F.R.S., of Dublin, has kindly undertaken to determine the electrical properties of the steel wire just mentioned, but the results are not yet completed. About twelve months ago the writer, thinking that silicon might confer upon iron qualities suitable for the manufacture of magnets, sent to Mr. Bottomley, in Sir W. Thomson's laboratory, Glasgow, a forged sample, containing 4·43 per cent of silicon and 0·18 per cent of carbon

(To be continued).

PREPARATION AND PROPERTIES OF ANHYDROUS PLATINUM BIFLUORIDE.

By H. MOISSAN.

In the researches undertaken hitherto for the isolation of fluorine, several *savants* have vainly sought to prepare platinum fluoride in the anhydrous state. It seemed according to the analogies of the fluorides and the chlorides, that platinum fluoride might be split up into platinum and fluorine by a mere rise of temperature. In 1856 M. Fremy wrote as follows:—"As for the gold and platinum fluorides, which would probably have given fluorine by ignition if I could have obtained them in an anhydrous state, it has been impossible for me to produce them by combining hydrofluoric acid with the hydrated oxides of gold and platinum."

That which was impossible—and we shall see below wherefore—on setting out from hydrofluoric acid and the hydrated oxides has become relatively easy on making use of platinum and fluorine. We have already had occasion, in our first researches on fluorine, to indicate that platinum is easily attacked by this body with the aid of heat.

We first determined at what temperatures platinum is attacked. When fluorine is really free from hydrofluoric acid, platinum in wire or foil is not attacked at 100°. For a decided formation of the compound a temperature of 500° to 600° is necessary. If platinum is immersed in a gaseous mixture of fluorine and hydrofluoric acid it is attacked more readily. It is the same when platinum remains in contact with liquid hydrofluoric acid saturated with fluorine, as in our electrolytic apparatus, in which case the platinum rod which serves as a positive electrode is rapidly corroded, even at a temperature bordering upon 0°.

As pure fluorine strongly attacks platinum at temperatures of 500° to 600°, in order to cause these bodies to combine it is merely requisite to heat to dull redness platinum kept in a current of fluorine gas. If the management of fluorine at common temperatures presents difficulties, it will be understood that the experiment requires some preparations. We take a bundle of platinum wires, which are introduced into a thick tube of platinum or into a tube of fluor-spar traversed by a rapid current of fluorine, and kept at dull redness. As soon as platinum fluoride is formed, the bunch of platinum wires is withdrawn from the apparatus and placed in a very dry glass tube. If the operation has been conducted in a platinum tube a considerable quantity of fluoride remains melted in the apparatus.

Platinum fluoride appears in melted masses of a deep red, or in small yellowish crystals resembling those of anhydrous platinum chloride in colour. It is very hygroscopic, and it cannot be preserved for some months without change, even in stoppered glass tubes which have been previously well dried. Its most curious reaction is that with water. If the fluoride is placed in a little distilled water in a platinum capsule there is at once produced a solution of a tawny colour, but almost immediately the liquid becomes heated the fluoride is decomposed, yielding hydrated platinic oxide and hydrofluoric acid. If the quantity of water is relatively large in proportion to the fluoride, and its temperature is low, the solution may be kept for a few moments without decomposition. As soon as the liquid is raised to a boil the above-mentioned decomposition is rapidly determined. This decomposition explains why it has hitherto been impossible to prepare the anhydrous platinum fluoride in the wet way. This compound cannot be produced in contact with water, as it rapidly decomposes that liquid, the fluorine uniting with the hydrogen to form hydrofluoric acid, and the platinum combining with oxygen to form a yellowish brown precipitate, soluble in potassa, and approximating in its properties to the hydrated bioxide of M. Fremy, PtO_2H_2O.

At redness, platinum fluoride is split up into fluorine and metallic platinum. This experiment may be made by heating to redness the fluoride obtained as above in a platinum tube closed at one end. If crystalline silicon is then placed at the open end of the tube the silicon takes fire at the common temperature, indicating distinctly the liberation of the fluorine. If the platinum resulting from this decomposition is examined it is found to be crystalline. This new instance may be added to those which occasioned M. Daubrée to call attention to the mineralising *rôle* of fluorine, which has since been confirmed by the fine mineralogical syntheses of H. Sainte-Claire Deville and M. Hautefeuille.

The analysis of platinum fluoride has been made by dissolving this salt in much cold water, decanting rapidly to remove the small quantity of insoluble platinous fluoride which is formed on contact with the metal. The liquid is then decomposed at the boiling-point. It is evaporated to dryness, ignited, and the composition of the fluoride soluble in water is deduced from the weight of the platinum. The analyses answer to the formula $PtFl_2$.

Gold, under the same conditions, yields a dark-coloured very hygroscopic fluoride, decomposable by heat into fluorine and metal.

In fine platinum difluoride $PtFl_2$ decomposes water at common temperatures. At a red heat it is resolved into crystalline platinum and fluorine. If this compound can be obtained by an indirect manner, which may possibly

be effected, it will be easy to have a preparation of fluorine based upon a purely chemical reaction.

As pure fluorine has no action upon platinum at common temperatures, it becomes possible to determine its physical constants. M. Moissan hopes soon to submit to the Academy new researches on the density, the colour, and the spectrum of fluorine.—*Comptes Rendus* (Vol. cix., p. 807).

ON THE REDUCTION OF ALUMINIUM.*

By Dr. WAHL

At the meeting on October 15th Dr. Wahl made some remarks on the industrial production of aluminium by electrolysis. He referred to the process of M. Adolphe Minet, in operation industrially at Creil (Oise), France, and which, in essential parts, was identical with that of Mr. Hall. Mr. Minet electrolyses a bath composed of forty per cent of cryolite and sixty per cent of chloride of sodium, maintained in the state of igneous fusion. The bath is continually regenerated by additions of alumina (or bauxite). The interesting point in considering the two processes, the speaker stated, was the different explanations of the operations taking place in the bath under the action of the electric current upon substantially the same components; Hall claiming that the alumina undergoes electrolysis, the solvent fluorides being unaffected, and Minet that the fluorides are electrolysed, the liberated fluorine acting upon the alumina, to form fresh fluoride, thus maintaining the bath. The explanation of M. Minet, the speaker held, to be the rational one.

NOTICES OF BOOKS.

Iron and Steel Manufacture. A Text-Book for Beginners. By Arthur H. Hiorns, Principal, School of Metallurgy, Birmingham and Midland Institute. London: Macmillan and Co.

This little work is to some extent intended for examinational purposes, since, in the preface, we are informed that "Pupils preparing for the ordinary grade examinations of the City and Guilds of London Institute will find the questions at the end of each chapter specially useful." Whether they have been selected from papers set on occasion of former examinations we are unable to say. The subjects taken up are treated briefly, of course, seeing that the entire work extends only to 180 pages, including the index, but clearly and correctly.

Very few passages require notice. It does not appear what is the exact nature of the "Belfast aluminous ore," described here as similar to bauxite. It quite disagrees in composition, according to the analysis given, with the "Eglinton alum clay" from the North-east of Ireland, which contains more alumina, more combined water, and very much less ferric oxide.

The residual matter from roasting iron-pyrites in the manufacture of sulphuric acid is here spoken of as "blue billy." In the Lancashire alkali district it is ordinarily named "burnt ore," whilst the name "blue billy" is commonly given to the spent lime from the gas-purifiers.

The masses of meteoric iron mentioned on p. 28 cannot be considered as the largest on record.

The illustrations, eighty in number, are well selected, and add much to the value of the book.

An Introduction to Chemical Science. By R. P. Williams, A.M. Edited and revised by B. P. Lascelles, M.A., F.C.S. London: Ginn and Co.

This is an ably written treatise, and may be recommended if, indeed, there is necessity or even room for any more elementary works on chemistry. It has the merit of making no reference to any code, syllabus, or examination. Its greatest deficiency is, in our opinion, the omission of the Periodic Law, which now forms so essential a feature in chemical theory. In the table of the principal elements we note that the author and editor still retain the old atomic weight for platinum, making it higher than that of gold.

A few other errors have escaped notice. Thus, we read that "Graphite is found in the oldest rock-formations in the United States and Siberia." Now, though graphite certainly occurs in the United States, to us in Britain the deposits of that mineral in Ceylon and in Bavaria are of greater importance.

In § 73 we note an un-English expression; the pupil is told to "touch a drop *to* the tongue, noting the taste." A correct writer would have said "*with* the tongue." Sulphuric acid, we read, is used in making "indigo and madder." Perhaps the author means the so-called extract of indigo.

It is stated that fashionable women sometimes eat arsenious acid "for the purpose of beautifying the complexion, to which it imparts a ghastly white unearthly hue." We fear that this evil habit is gaining ground both in America and on the European Continent. How anyone can think a ghastly complexion beautiful we fail to see. The injurious effects of arsenical wall papers here mentioned as doubtful have unfortunately become past all doubt, though the idiosyncrasy of persons exposed to their influence plays here a great part.

Under alcohol it is mentioned that the American courts now regard all liquors having three per cent or less of alcohol as not intoxicating. In Massachusetts it (the limit) is one per cent. If such were the rule in Britain, most of the "temperance" beverages sold would come under the jurisdiction of the excise.

The Clinical Use of Prisms and the Decentering of Lenses. By Ernest E. Maddox, M.B. Bristol: Wright and Co. London: Hamilton, Adams, and Co.

This work cannot well be considered to fall within our cognisance, as its merits can only be estimated by the practical ophthalmic surgeon. The author discusses in the first place prisms from the geometrical, the optical, and the clinical point of view. He then passes on to "marking the apex," prismetry, planeness of surface, adjustment in trial frame, and temporary trials. He then takes up the decentering of lenses, localisation, the analysis of spectacles, and the chief clinical applications of prisms, viz., in the consulting-room and in spectacles.

The Geological Record for 1880—1884 (inclusive): A List of Publications on Geology, Mineralogy, and Palæontology Published during those years; together with certain References Omitted from Previous Volumes. Edited by W. Topley, F.R.S., F.G.S., and C. D. Sherborn, F.G.S. Vol. II., Physical and Applied Geology, Petrology, Meteorites, Mineralogy, Mineral Waters, Palæontology, General, Maps, and Sections. London: Taylor and Francis.

This volume will be of the greatest value to geologists, especially if desirous of knowing what has been done in any particular department of their science, but as it contains no abstracts of the memoirs indexed it cannot be reviewed.

Annual Report of the Board of Regents of the Smithsonian Institution: Showing the Operations, Expenditure, and Conditions of the Institution for the Year ending June 30th, 1886. Part I. Washington: Government Printing Office, 1889.

Whilst this Report gives proof of abundant and valuable work in other departments of science, chemistry has

* From the Chemical Section of the *Journal of the Franklin Institute*, Nov., 1889

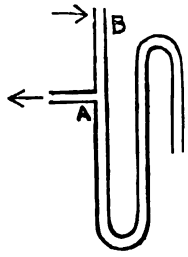
not fared nearly so well as, *e.g.*, ethnology. We find here no chemical matter, except a brief notice of the researches on the venom of serpents, by Messrs. Mitchell and Reichert: no details are given.

CORRESPONDENCE.

WATER-BATH REGULATOR.

To the Editor of the Chemical News.

SIR,—In the last issue of the *Chemiker Zeitung* an abstract appears of an article from your valued journal describing Mr. Easterfield's water-bath regulator. It may possibly interest you to know that I recently devised an arrangement for the same purpose very similar to the above; but, I think, more easily extemporised. Mine is of lead pipe, with an ordinary brass T-piece at A.



Water enters from a small elbow tube loosely resting on B, but without closing the latter. The exit is at A, which must be at the water-level to be maintained in the bath; this level may be easily altered, when desired, by bending the pipe.—I am, &c.,

CHARLES E. SOHN, F.C.S., A.I.C.

25, Beverley Road, Anerley, Surrey,
December 9, 1889.

STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION.

To the Editor of the Chemical News.

SIR,—The use of ferrous ammonium sulphate in the production of standard iron solutions for titration is not new. Mr. French will find it in Sutton's "Volumetric Analysis," published as far back as 1863.—I am, &c.,

H. N. D.

Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 22, November 25, 1889.

Animal Heat. Heat developed by the Action of Oxygen upon the Blood.—M. Berthelot.—When Lavoisier recognised that animal heat is essentially a phenomenon of combustion, he raised the question whether this combustion takes place in the lungs themselves at the point where the oxygen is absorbed and the carbonic acid given off, or if it is produced in the entire system, the absorption of the oxygen taking case in virtue of a first reaction effected at the expense of the blood. M. Berthelot now finds that the animal heat may be resolved into two portions; one part, about the seventh, is produced in the lungs themselves by the fixation of oxygen, whilst the remaining six-sevenths are developed in the system by reactions of oxidation and hydration. The absorption of oxygen tends to raise the temperature of the blood in the lungs, whilst the return of the carbonic acid to the gaseous state and that of watery vapour tend to lower it.

Exhaustion of Soils by Cultivation without Manures, and the Utility of the Organic Matter of the Soil.—P. P. Dehérain.—The author is led to admit that the organic matter of the soil serves directly as a plant-food. He compared experimentally the vegetation of sugar-beets in a soil rich in organic matter and in a soil poor in humus, but watered and mixed with nitrates, phosphates, and salts of potassium. He took two large earthenware pots, varnished externally, and capable of holding 30 kilos. of soil, and filled them, the one with a soil rich in humus, the other with an exhausted soil. The poor soil was watered and received the addition of 3 grms. sodium nitrate, 3 grms. of calcium superphosphate, and the same weight of potassium chloride. A single beet was allowed to remain in each. The beet which had grown in the rich soil weighed 730 grms.; the root alone, 410; the sugar in 100 parts of the juice, 15·04; and the total sugar, 61·60 grms. The plant grown in the poor soil which had received the mineral manures weighed only 165 grms.; the root alone, 92; the percentage of sugar was 11·11; and the entire weight of sugar, 10·12 grms. The simplest interpretation of the facts seems to be that the organic matter forms a necessary part of the food of the plant, just as do the nitrates, the phosphates, and the potash, and that its absence is as prejudicial as that of any of these mineral constituents.

Preparation and Properties of Anhydrous Platinum Fluoride.—H. Moissan.—This paper will be inserted in full.

A Contribution to the Study of Double Decompositions between the Haloid Salts of Mercury and of Zinc.—Raoul Varet.—The action of mercury cyanide upon zinc bromide and that of zinc cyanide upon mercury lead to the system ($HgCy.HgBr.ZnCy + HgB$). The production of the triple salt $HgCy.HgBr.ZnCy + 8HO$ leads to an equilibrium which limits the inverse reactions which might reproduce one of the original systems, whether $Hg_2Cy_2 + Zn_2Br_2$, or, on the contrary,—

$$Hg_2Br_2 + Zn_2Cy.$$

All the zinc cyanide does not take part in the formation of the triple salt, and the quantity which enters into combination depends both on the proportion of water and the proportion of mercury cyanide dissolved therein.

A New Sugar with an Aromatic Nucleus.—M. Maquenne.—The two pinites, and probably also sennite, are closely connected with the aromatic series, and form ethers derived from a new principle, isomeric with the glucoses, and which appears to answer to the same formula as inosite.

Synthesis of Metaphenylene Diamine from Resorcine and Ammonia.—Alphonse Seyewitz.—Below 150° resorcine and ammonia do not react; the amine is only formed at upwards of 200°, the yield of diamine increasing with the temperature. Below 250° resorcine remains always unattacked.

Action of Heat upon Chloralammonium.—A. Béhal and M. Choay.—This paper does not admit of useful abstraction.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. vi., No. 2.

Determination of Sulphur in Burnt Pyrites.—The process of Watson is mentioned as simple, practical, and fairly accurate. The directions given are to mix 2 or 3 grms. of the ore finely ground with 1 or 2 grms. of sodium

hydrocarbonate of known alkalimetric value, and heat the mixture for five to ten minutes in a crucible of porcelain, nickel, or platinum. The mixture is then stirred up and heated again more strongly for fifteen minutes. Lastly, the mass is extracted with boiling water, filtered, and the excess of alkali determined volumetrically by means of normal hydrochloric acid, using methyl-orange as indicator.

MISCELLANEOUS.

An Appeal.—Mr. G. F. Rodwell, after twelve years of good service at Marlborough College, was struck with paralysis and aphasia in 1883, and has since then been utterly incapacitated for work of any kind. He had, for a long period, helped to support an invalid mother and sister, and his seizure is attributed in part to extra work undertaken, both in term and vacation, for this object. In the hope of recovering his general health and nervous power, Mr. Rodwell has undertaken voyages to America and elsewhere, which have utterly failed to restore him, but have exhausted the larger part of his savings; so that he is now left with a bare £300 of capital, and no other source of income, while he has no kinsfolk able to maintain him. The Council of the College made him a grant of 200 guineas in 1883, and have recently voted him £50, with an intimation that they will again consider his application at the end of twelve months. He had long cherished a hope that in consideration of his scientific and literary labours a pension might be awarded to him from the Civil List; and every effort was made to recommend him for such a pension; but the hope of it has now been finally abandoned. Under these painful and exceptional circumstances it is thought that many of Mr. Rodwell's old friends and pupils will be ready to show their sympathy for him by contributing to a fund for the purchase of a small annuity on his life. Contributions may be sent to The Master, The Bursar, or M. H. Gould, Esq., Marlborough College, or to his sister, Miss Rodwell, Parkbrook, Hampton-on-Thames.

Royal Institution.—The following are the Lecture Arrangements before Easter:—

Professor A. W. Rücker, Six Christmas Lectures to Juveniles, on "Electricity."

Professor G. J. Romanes, Ten Lectures on "The Post-Darwinian Period."

Mr. E. Roscoe Mullins, Three Lectures on "Sculpture in relation to the Age."

The Rev. Canon Ainger, Three Lectures on "The Three Stages of Shakspeare's Art."

Mr. Frederick Niecks, Four Lectures on "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations).

Professor Flower, Three Lectures on "The Natural History of the Horse and of its Extinct and Existing Allies."

The Right Hon. Lord Rayleigh, Seven Lectures on "Electricity and Magnetism."

The following are the arrangements for the Friday Evening Meetings:—

Jan. 24th. Professor Dewar, M.A., F.R.S.—"Scientific Work of Joule."

Jan. 31st. Sir Frederick Abel, C.B., D.C.L., D.Sc.—"On Smokeless Explosives."

Feb. 7th. Henry B. Wheatley.—"The London Stage in Elizabeth's Reign."

Feb. 14th. Professor J. A. Fleming.—"Problems in the Physics of an Electric Lamp."

Feb. 21st. Shelford Bidwell.—"Magnetic Phenomena."

Feb. 28th. Professor C. Hubert H. Parry.—"Evolution in Music."

March 7th. Francis Gotch.—"Electrical Relations of the Brain and Spinal Cord."

March 14th. Professor T. E. Thorpe.—"The Glow of Phosphorus."

March 21st. Professor G. F. Fitzgerald.—"Electromagnetic Radiation."

March 28th.—The Right Hon Lord Rayleigh.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Nickel and Cobalt.—Would you inform me through your correspondence in the Chemical News which is the best standard metallurgical work on nickel and cobalt?—Nickel.

MEETINGS FOR THE WEEK.

Monday, Dec. 16th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30
Wednesday, 18th.—Society of Arts, 8. "London Sewage," by Sir Robert Rawlinson, K.C.B.
—— Meteorological, 7.
—— Geological, 8.
Thursday, 19th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8. "On Frangulin," by Prof. Thorpe, F.R.S., and H. H. Robinson, M.A.

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THE CHEMICAL NEWS.

Vol. LX. No. 1569.

SOME PENDULUM EXPERIMENTS IN RELATION TO THE MUTUAL APPROACH OF THE BODIES, AND A SUGGESTION AS TO THE CAUSE OF THAT APPROACH.

By J. BAYNES THOMPSON.

Mutual attraction is said to cause that approach, but I can find no one who can conceive a possible mode of the action of attraction; how one piece of crude matter can reach across space and pull another piece of matter towards itself. Absurd as that appears, it is just what attraction means if it has any meaning at all. No one has ever proved by experiment or by reason from experiment that there is such a thing as attraction. All that experiment has proved to our senses is that bodies do tend to approach. The how is a deduction of reason which has not been made.

The general opinion of physicists may be obtained from "Ganot's Physics." It is that universal attraction is a force in virtue of which the material particles of all bodies tend incessantly to approach each other. *The nature of the force is entirely unknown.* We are at a loss whether to consider it as a general property inherent in matter, or whether the effects of which it is the cause are due to the action of some external agent. *It is a mutual action, however, which all bodies at rest or in motion exert upon one another*, no matter how great or how small the space between them may be, or whether the space be occupied or unoccupied by other matter. . . . . "The attraction between any two bodies is the resultant of the attraction of each molecule of the one upon every molecule of the other according to the law of Newton, which may be thus expressed.

"*The attraction between two material particles is directly proportional to the product of their masses, and inversely proportional to the squares of their distances asunder.*

"To illustrate this we may take the case of two spheres which, owing to their symmetry, attract each other just as if their masses were concentrated in their centres. If, without other alteration, the mass of one sphere were doubled, trebled, &c, &c., the force will be doubled, trebled, &c. If, however, the mass of one sphere being doubled, that of the other were increased three times, the distance between their centres remaining the same, the attraction would be increased six times."

This statement is rather contradictory. It begins with the statement that the nature of the force of attraction is "*entirely unknown*"; but further on it states that it is a mutual action, however; so that, according to that, the nature of it is not entirely unknown. Further, it states:—"We are at a loss whether to consider it a universal property inherent in matter, or whether the effects of which it is the cause are due to the action of some external agent." That is not very clear, but it appears to mean that it is not known whether the cause is mutual attraction or external pressure. Yet, immediately after, it is stated that each particle of matter attracts every other particle of matter, each directly according to its mass, and gives examples as illustrations, just as if everything was known about it.

The latest statement on this matter is by Professor Young in his "Text-book of General Astronomy" published this year (1889) in Boston, U.S.A. Under the heading "Gravity" he says:—"The law of gravitation discovered by Newton declares that any particle of matter attracts any other particle with a force (stress if the bodies are prevented from moving) proportional to the inverse squares of the distance between them, and directly to the product of their masses; or, as a formula, may be written—

$$FK\frac{m_1 \times m_2}{d_2}.$$

m_1 and m_2 are the masses, d the distance, F the force, and K a constant numerical factor depending on the units employed. He then makes the following remarks:—

"We must not imagine the word 'attract' to mean too much. It merely states the fact that there is a *tendency* for the bodies to move towards each other, without including or implying any explanation of the fact. So far no explanation has appeared which is less difficult to comprehend than the fact itself. Whether bodies are *drawn together* by some outside action or pushed together; or whether *they themselves can act across space with mathematical intelligence*—in what way it is that 'attraction' comes about is still unknown. Apparently as inscrutable as the very nature and constitution of an atom of matter itself. *It is simply a fundamental fact.*"

Evidently Professor Young did not well consider these remarks before he put them down. He begins by saying that attraction does not mean attraction at all, when he has just written down the law of mutual attraction and given a formula by which to calculate the force of attraction. Then he says we do not know whether bodies are drawn together by some outside action, but an outside action or force could act only by pushing. The next suggestion is unique as an attempt to explain mutual attraction. He says we do not know whether matter may not be able to act across space with mathematical intelligence!

Just think! Metals, stones, and brickbats may have mathematical intelligence! Of course that only means that Professor Young cannot comprehend mutual attraction any more than anyone else. Still, as a final remark he says:—"*It is simply a fundamental fact.*" Now, how can Professor Young know that it is a fundamental fact, or even a fact at all? since he confessedly comprehends nothing about it. Clearly no assistance can be derived from the opinions of scientists on this matter. The only resource remaining is experiment, to see if any light can be obtained from the facts.

For the purpose of these experiments I have imagined several modifications of Cavendish's apparatus; but the manipulation was so difficult, and it was not easy to get the weight corresponding with the torsion; moreover, the torsion was not constant in any wire that I used. Therefore I devised a pendulum apparatus, and had it made. It is very steady and easy to manipulate; moreover, with it the force acts against gravity; consequently it is easy to calculate. For example, take the pendulum at the perpendicular; gravity is then annulled by the support of the pendulum rod. Now raise the pendulum through 90°, and the full force of the weight of the bob and half the weight of the rod will be exerted, and at every angle from that to the perpendicular the weight will be proportional to the vers-sine of the angle of divergence from the perpendicular, and the vers-sine is easily found.

Take the pendulum as radius r, angle of divergence
Then r − co-sine = vers-sine.

Now let weight of bob, &c., be Wt, and force causing the deviation F, and the force is found as follows:—

$$r : \text{vers-sine} :: \text{Wt} : F = \frac{\text{vers-sine} \times \text{Wt}}{r} = F.$$

The actual apparatus has the following parts and dimensions. The pendulum is 42 inches long; it works on a steel knife-edge, and has a needle at the bottom as pointer. Below this there is a micrometer. The screw of this micrometer has twenty threads to the inch. It works in a bearing at one end, having a collar to keep it

in its place; at the other it moves on a pivot which has a set screw to keep it in its place when screwed up, so that the micrometer screw may not shake. On the micrometer screw there is a block with a needle fixed in it, which can be placed under the pendulum needle, point to point. The shaft of the screw passes through the side of the case and through a dial placed outside. This dial has upon it a circle of 5 inches circumference. Each inch is divided into 10 parts. At the end of the screw-shaft is fixed a head with a needle in it as pointer, so that when this pointer moves over $\frac{1}{10}$ inch, the needle in the block on the screw moves over one-thousandth of an inch. It would be easy to measure 1-2000th of an inch by moving the pointer over half a tenth, but that length could scarcely be perceived at the micrometer needle. As pendulum bobs I have cylinders of lead, one 2½ in. diameter and 2½ in. long, the other 2½ in. diameter and 5 inches long. They have $\frac{1}{16}$ in. holes through them, both longitudinally and transversely, so that they can be mounted vertically and horizontally; their weights are 5 lbs. and 10 lbs. The pendulum rod weighs 8½ ozs., but the bob-half of the rod weighs 4 ozs. and the head-end 4½ ozs. on account of the steel head and only a needle at the other end. The pendulum rod is a light brass tube. Besides the two cylinders mentioned there are two other similar cylinders to place stationary opposite the bob; they are also 5 lbs. and 10 lbs. weight and 2½ in. diameter, 2½ in. and 5 in. long. The case stands on levelling screws.

The mode of using the apparatus is as follows, it having been first levelled:—

The pendulum is steadied and allowed to come to rest; then the micrometer screw is turned till the point of the needle comes opposite the point of the pendulum needle, and the place of the pointer on the dial is noted. The required cylinder is placed opposite the bob of the pendulum at $\frac{1}{32}$ in. from it. The cylinder is placed vertical if the bob be vertical, and horizontal if the bob be horizontal. The pendulum will be found to have moved towards the fixed cylinder. When it has come to rest the micrometer screw is turned till the point of the needle is again opposite the point of the pendulum needle and the position of the pointer on the dial is noted. The difference between the two positions of the pointer on the dial shows the length of arc the pendulum has passed over, and this gives the angle of deviation from the perpendicular.

The following table shows a series of eight experiments, which have been repeated many times with but little variation.

Position.	Cylinder on pendulum.	Cylinder fixed.	Arc passed over in inches.	Angle of deviation.	Force in m.grms.
	Lbs.	Lbs.			
1. Vertical ..	5	5	0·013	1′3″5	28·353
2. ,, ..	5	10	0·013	1′3″5	28·353
3. Horizontal..	5	5	0·013	1′3″5	28·353
4. ,, ..	5	10	0·026	2′7″0	56 707
5. Vertical ..	10	10	0·013	1′3″5	56·245
6. ,, ..	10	5	0·007	34″	28·670
7. Horizontal..	10	10	0·013	1′3″5	53·245
8. ,, ..	10	5	0·007	34″	28·670

Now let us try to interpret these experiment, first as to the cause of approach being mutual attraction, and then as to what they point to as the real cause of approach. No. 1 is 5 lbs. and 5 lbs. vertical, the measured arc passed over by pendulum is 0·013 in. and calculated force 28·353 m.grms. No. 2 is 5 lbs. and 10 lbs. vertical, the arc passed over and calculated force the same as with the two 5 lb. cylinders; but this is a 5 lb., and a 10 lb., therefore, ought to be double if caused by mutual attraction.

Now take No. 4, the same two cylinders as No. 2, but placed horizontally—that is, end to end—the pendulum bob being 5 lbs. as before. The measured arc that the pendulum has passed over is just double and the calculated force just double. This cannot be caused by mutual attraction, as the masses are the same as before; but it is simply from position.

No. 5 is 10 lbs. and 10 lbs. Here the arc passed over is the same as that passed over with the 5 lbs. and 5 lbs., but the masses being nearly double, namely, 5½ to 10½ on the pendulum, the force is nearly double. But the products of their masses are nearly as one to four; therefore, if the law of mutual attraction were true, the force should be nearly four times.

No. 6, the fixed cylinder, is about half the preceding cylinder; the arc is 0·007 instead of 0·0065, but the dial showed 0·007. We put it back half-a-tenth, but, with the naked eye, could not discern the difference at the micrometer needle; therefore we left it at 0·007 by calculation; that of course showed a little more than half. No. 7, 10 lbs. and 10 lbs. end to end; they gave the same as when side by side. No. 8, 10 lbs. and 5 lbs.; this gave the same as No. 6, when the cylinders were side by side.

According to these experiments there is no such thing as mutual attraction; therefore bodies mutually approach each other if free to move, from some other cause. As that cause I would suggest the pressure of the ether. Two bodies being free to move and near enough to each other, they each screen the other from the opposite bombardment of the ether by so much as their molecules stop the streams of ether molecules from passing through them; and these experiments seem to point to that as the cause. In No. 1 the cylinders were equal. In No. 2 the fixed cylinder is double what it is in No. 1, but the approach and force are the same. They are side by side vertically and their centres are opposite; but the larger cylinder can screen the smaller only to the size of the smaller, the parts of the larger cylinder above and below the smaller having no effect on the smaller cylinder. No. 3, 5 lbs. to 5 lbs. end to end, screen each other as before, being 2½ in. through each way. No. 4, 5 lbs. to 10 lbs. end to end. The force here is double that of 2½ and 2½, because the 5 in. cylinder screened the 2½ inch double. The other four experiments show the same thing; viz., that in proportion as the fixed cylinder screens the movable one, so is the force that causes the movable one to approach the fixed one.

As to the inverse squares, I have made some experiments on that also. The following table shows them. I took the 5 lb. cylinder on the pendulum and the 10 lb. cylinder fixed, because they give the greatest angle of deviation:—

Inches apart.	Arc passed over. Inches.	Force in M.grms.
$\frac{1}{32}$	0·026	56·707
$\frac{1}{8}$	0·024	52·345
$\frac{1}{4}$	0·023	50·164
$\frac{1}{8}$	0·022	47·983
$\frac{3}{4}$	0·021	45·802
1	0·020	43·621
1½	0·019	41·440
1⅛	0·018	39·259
1¾	0·017	37·078
2	0·016	34·897
2¼	0·015	32·716
2⅛	0·014	30·535
2¾	0·013	28·354
3	0·012	26·173
3¼	0·011	23·992
3½	0·010	21·811

In this table there does not appear to be any ratio between the distance apart, the arc passed over, and the corresponding force. However, it is certainly not as the inverse squares of the distance asunder.

The Methods of Teaching Chemistry.—We are informed by the Secretary of the Committee appointed by the British Association to enquire into the methods at present adopted in teaching chemistry that their second Report, made at the recent Newcastle Meeting, has now been put on sale by the Council. It may be obtained from the office of the Association, 22, Albemarle Street, W.

OSMOTIC PRESSURE:

With Special Reference to the Work of Rüdorff and Raoult.*

By EMILY J. LLOYD.

(Concluded from p. 286).

In 1883, M. F. M. Raoult, Professor of Chemistry at Grenoble, took up the subject (see *Annales de Chimie et de Physique*, 1883, 1884, 1885, 1886).

He examined first the freezing-point of solutions of some thirty organic substances, representatives of the various groups, except hydrocarbons — monatomic and polyatomic alcohols, sugars, glucose, phenols, aldehyds, acids, ethers, amides, amines, &c. These bodies differ as much in solubility and molecular weight as in chemical properties. The *coefficients of depression* of the freezing-points range from 0·052 to 1·117 (proportion 1 : 21½); but the *molecular depression* approximates, in most cases, to somewhere about 19. Hence, Raoult concludes that:—

1. The molecules of different organic matters dissolved in the same quantity of water cause approximately the same depression in the freezing-point of the solvent.

2. The constitution of the body exerts a feeble though evident influence on the freezing point. But the depression depends more on the nature of each atom than on the place it holds in the compound (for acids the constant approximates to 19, for sugars to 18, for alcohols to 17). From this Raoult calculates that there should be fixed coefficients for each element. He found these to be: for H 15, for C 15, for O 30, for N 30.

Then for any substance, $C_pH_qN_rO_s$, the molecular depression is—

$$\frac{15p+15q+30r+30s}{p+q+r+s}.$$

In cases where the vapour density of a compound cannot be determined, Raoult claims this method to be of great importance in determining the molecular weight; he decides in favour of that number *which multiplied by the coefficient of depression approaches most nearly to* 19.

Thus, in the case of oxalic acid, the molecule must be one of the following:—

$$CHO_2=45,\ C_2H_2O_4=90,\ C_3H_3O_6=135,\ \&c.$$

The calculation for the molecular depression is—

$$\frac{15n+15n+2\times30n}{4n} = \frac{90}{4} = 22{\cdot}5.$$

Experiment gives for the coefficient of depression 0·255. Now, if M = the molecular weight,

$$M\times0{\cdot}255=22{\cdot}5,$$

whence—

$$M=88{\cdot}3;$$

i.e., among the above possible formulæ we choose the second, the molecular weight of which approaches most nearly to 88·3.

The calculated number does not always agree very closely with the observed. Raoult gives this explanation; "The molecules of an organic compound seem simply separated by the act of solution. As vaporisation does not completely separate the molecules of a body, so, in all probability, neither does solution."

Raoult next (*Ann. de Ch. et de Phys.*, 1884) published the results of his investigations on other solvents.

1. *Acetic Acid.*— Of the fifty-nine substances, mostly organic, with which Raoult experimented, the molecular weights varied from 18 to 690. The coefficients of depression ranged between 0·062 and 1·830; but in fifty-six cases the product M A (where M = molecular weight, A = coefficient of depression) approximated to 38.

In the three other cases (sulphuric and hydrochloric acids and magnesium acetate) M A = very nearly 18.

2. *Formic Acid.*—Raoult made fewer experiments with this solvent, but he found that the coefficients of depression, as before, varied considerably, 0·067 to 0·593, while the product M A in every case but one (that of magnesium formate) approched the number 28; for magnesium formate it was 13·9.

3. *Benzene.*— In this case the maximum molecular depression for some forty-two substances is about 50. With the hydrocarbons and their derivatives, ethers, aldehyds, acetones, nonoxygenated acids, and metallic chlorides M A = 49. With alcohols, phenols, and acids containing the group OH, the molecular depression approaches a mean of 25, just half the other number, as noticed with acetic and formic acids as solvents.

4. *Nitrobenzene.*—The same law is seen to obtain in this case. For thirteen out of the eighteen substances dissolved M A is never higher than 73·6, and approaches the mean 71; this for hydrocarbons and their substitution derivatives, ethers, aldehyds, acetones, chlorides of the metalloids; but, as with benzene for solvent, alcohols and acids containing the hydroxyl group, give a product, M A, rather more than half that in the other cases.

5. *Ethylene Di-bromide.*—

	A =	M A =
For CS_2	1·534	116·6
,, $CHCl_3$	0·991	118·4
,, C_6H_6	1·528	119·2
,, $(C_2H_5)_2O$.. ..	1·588	117·5
,, $AsCl_3$	0·650	118·1
,, $C_2H_4O_2$	0·961	57·7
,, C_2H_5OH	1·234	56·8

Raoult concludes his second paper with the following generalisations:—

1. Every body in solution, liquid or gaseous, lowers the freezing-point of its solvent.

2. There is for each solvent a maximum lowering.

3. Every solution has two constants, the one double the other.

4. Whatever be the nature of the mutual action of the solvents, it is approximately the same for all solvents.

This statement requires some explanation. To consider the action of one molecule of the dissolved substance on one molecule of the solvent we must divide the molecular depression by the molecular weight of the solvent. We then get the remarkably coincident numbers:—

For [water	$\frac{47}{18}$ = 2·61]
,, formic acid	$\frac{28}{46}$ = 0·63
,, acetic acid	$\frac{38}{60}$ = 0·65
,, benzene	$\frac{49}{78}$ = 0·64
,, nitrobenzene	$\frac{74}{123}$ = 0·59
,, ethylene di-bromide.	$\frac{110}{188}$ = 0·63

i.e., The action of the *solvent* is independent of its nature —a result which might be expected from the fact that the action of the dissolved substance depends, not on the nature or arrangement of the atoms which compose the molecule, but on the number of the molecules. Another way of stating this is:—

Lowering of the freezing-point of a solution =

$$0{\cdot}63\times\frac{\text{No. of molecules of substance}}{\text{,, ,, solvent}}.$$

Water gives the number 2·61 as a maximum. From various considerations, Raoult afterwards concluded that the water molecule is really double the steam molecule, H_2O.

The above statements refer to organic substances only. For inorganic substances the numbers found by Raoult varied between 34 and 46. He therefore undertook further researches on their solutions in water. The results were published in the *Ann. de Ch. et de Phys.* for 1885.

The first noticeable regularity is the relation between similar salts of monad and diad metals of monatomic and polyatomic radicles.

* A Paper read before the Mason College Chemical Society, October 16, 1889.

				Difference.
Ba_2OH	49·7	2KHO	70·6	20·9
Ba_2ClO_3	44·1	$2KClO_3$	66·4	22·3
Ba_2NO_3	40·5	$2KNO_3$	61·6	21·1
$Ba_2PH_2O_2$.. ..	50·7	$2KPH_2O_2$	72·2	21·5
$Ba_2C_2H_3O_2$ ..	49·2	$2KC_2H_3O_2$	69·0	19·8
$BaCl_2$..	48·6	2KCl	67·2	18·6
BaI_2	51·0	2KI	70·4	19·4
$MgSO_4$	19·2	$2K_2SO_4$	39·0	19·8
$MgCrO_4$	19·5	K_2CrO_4	38·9	19·4
$MgC_4H_4O_4$ ..	23·9	$K_2C_4H_4O_4$	45·1	21·2
$BaC_4H_4O_5$.. ..	20·1	$K_2C_4H_4O_5$	41·9	21·8
		Mean difference ..		20·7

				Difference.
$\frac{1}{2}K_2SO_4$	19·0	KCl	33·6	14·6
$\frac{1}{2}MgSO_4$	9·6	$\frac{1}{2}MgCl_2$	24·4	14·8
$\frac{1}{2}K_2CrO_4$	19·4	KCl	33·6	14·2
$\frac{1}{2}MgCrO_4$	9·7	$\frac{1}{2}MgCl_2$	24·4	14·7
$\frac{1}{2}K_2SO_4$	19·0	KNO_3*	30·8	11·8
$\frac{1}{2}Al_{23}SO_4$	7·4	$\frac{1}{2}Al_{23}SO_4$	21·5	14·1
$\frac{1}{2}Al_{23}SO_4$	7·4	$\frac{1}{2}Al_{26}NO_3$	21·6	14·2
		Mean difference ..		14·0

i.e., Between the lowering produced in 100 grms. water by equal quantities of salts of the alkalies and alkaline earths there is a difference constant and equal to 10·5.

Also between the lowering produced by a monobasic acid and the corresponding salt of a dibasic acid there is a constant difference = 14.

1. From various reasons Raoult thinks that in a compound each atom exercises its own influence.

2. From consideration of the Tables above, he concludes that there is a constant proportion between the "partial depression" due to the electro-positive and electro-negative radicles of the same atomicity. For instance—

$$\frac{\text{Depression due to K}}{\text{,, ,, Cl}} = \frac{\text{Depression due to Mg}}{\text{,, ,, } SO_4}.$$

If we accept this hypothesis, we may re-write the equation thus—

$$\frac{\text{D. due to Mg}}{\text{,, } SO_4} = \frac{\text{D. due to K} - \text{D. due to } \frac{Mg}{2}}{\text{,, ,, Cl} - \text{,, ,, } \frac{SO_4}{2}}$$

$$\text{and this} = \frac{10{\cdot}5}{14};$$

Also—

D. due to $MgSO_4$ = D. due to Mg + D. due to SO_4 = 19.

From these two equations we find—

Depression due to Mg = 8·1
,, ,, SO_4 = 10·9

Similarly—

,, ,, Na = 15·0
,, ,, Cl = 20·0

By similar calculations Raoult finds the partial depression due to each atom, and sees that they group under four heads.

Group.

1 contains electro −ve radicles, monatomic At. Dp. = 20
2 ,, ,, ,, ,diatomic ,, = 11
3 ,, electro +ve radicles, monatomic ,, = 15
4 ,, ,, ,, ,diatomic ,, = 8

Having obtained these theoretical numbers it remains to see if they agree with the actual lowering produced. Raoult gives the following instances :—

	Calculated.	Observed.
KHO	35	35·3
Ba_2HO	48	49·7
HCl	35	36·7
NaCl	35	35·1
$BaCl_2$	48	48·6
$SnCl_4$	88	96·3
Al_2Cl_6	128	129·0
HNO_3	35	35·8
$NaNO_3$	35	34·0
Ba_2NO_3	48	40·5
$Al_{26}NO_3$	128	129·0
H_2SO_4	41	38·2
K_2SO_4	41	39·0
$MgSO_4$	19	19·0
$Al_{23}SO_4$	41	45·0

In a still later paper (*Annales de Chimie et de Physique*, July, 1886), M. Raoult has drawn the curves for the lowering of various salt solutions. In all cases he finds this rule to hold good :—

Trace the coefficient of lowering of the anhydrous substance to C = −1° to C = −4°, produce the part which is a straight line till it cuts the ordinate; this value multiplied by the molecular weight gives the molecular lowering.

Thus, if C′ and C″ be the abscissæ, $\frac{C'}{P'}$ $\frac{C''}{P''}$ be the ordinates of any two points on the line, the length of ordinate cut off by the line will be—

$$\frac{\frac{C''}{P''}\ \frac{C'}{P'} = \frac{C'}{P'}\ \frac{C''}{P''}}{C'' - C'}$$

= 19 for organic salts
= 34·6 for salts containing monatomic bases + monatomic acids.
= 39·8 for salts containing monatomic bases + monad acids.
= 45·2 for salts containing diad bases + monad acids.
= 17 ,, ,, ,, + diad ,,
= 130 for chlorides of hexatomic radicles.

If, however, we work with dilute solutions, so that the freezing-point does not go much below −1°, a single determination suffices, and for practical purposes we have—

$$\text{Molec. lowering} = \frac{C}{P} \times M.$$

The employment of dilute solutions has other advantages :—1. Avoidance of arbitrary conclusions as to state (anhydrous or variously hydrated) of the body in solution. 2. Production of an appreciable quantity of ice without sensibly modifying concentration of solution. 3. The thermometer remains stationary a longer time.

It will be thus seen that Raoult's method affords a valuable means of determining :—

1. The molecular weight of a substance in the dissolved state.
2. The basicity of an acid.
3. The atomicity of a metal.

Among recent applications we may notice :—

1. Messrs. Brown and Morris on the carbo-hydrates (*Journal of the Chemical Society*, June, 1888). They show that the formula for cane-sugar, maltose, and milk-sugar is $C_{12}H_{22}O_{11}$ = 342; for dextrose, invert-sugar, arabinose, and mannitol $C_6H_{12}O_6$ = 180, and not multiples of these numbers.

2. Professor Ramsay on nitric peroxide (*ibid*). The supposed formula is N_2O_4 = 92. The number found for solution in acetic acid = 93·8

3. Dr. Morris Loeb, on iodine in differently coloured solutions (*ibid*, Oct., 1888). Dr. Loeb worked by the vapour-tension method. The same influence which lowers the freezing-point also raises the boiling-point. His conclu-

* In experiments with this salt I obtained for molecular lowering 34, making difference = 15, a number which accords fairly well with other differences.

sion is that molec. of iodine in reddish brown ethereal solution $= I_4$, in violet solution a less complex molecule.

Turning, now, to the more *physical* side of the question:—

If we have a tube, closed at the bottom by a membrane, pervious to water, but not to sugar, and this tube be partially filled with a solution of sugar, and then placed in an outer vessel of water. The solution will draw the water through the membrane; the level of the liquid inside the tube will be considerably higher than that *outside* the tube. This will not continue indefinitely, but the quantity of water drawn in will vary with the concentration of the solution; or,

Suppose an ordinary unglazed porcelain cell half filled with a solution of known percentage composition, and provided with a piston, and this be immersed in a vessel of water. Ordinarily speaking, the water would press into the inner vessel, but by applying external force to the piston, not only may water be prevented entering, but even some of that already in may be driven out. The force thus applied can be measured.

If just sufficient force be applied to prevent water either entering or leaving the inner tube, then this force must exactly balance the *osmotic pressure* due to the substance dissolved.

Pfeffer describes such experiments and finds that—

1. At constant temperature, pressure is proportional to concentration.

2. If quantity of sugar be constant, pressure × vol. of water = constant.

3. If pressure be constant, vol. × abs. temperature = constant.

I.e., For changes in temperature and density *osmotic* pressure varies in the same way as pressure in a gas, or that Boyle's and Charles's laws can be applied to solutions as well as to gases.

Similarly with Avagadro's law—so far as can be shown by direct experiments with semi-pervious membranes—unit volumes of solutions of equal molecular content have the same osmotic pressure, which is equal to the pressure of unit volume of a gas of the same molecular contents.

(This applies to weak solutions only, just as gaseous laws apply to perfect gases only, in which the molecules are so far apart that action between them may be neglected).

From these and other considerations — diminution of vapour-tension, &c., — Van't Hoff has concluded that *the condition of molecules in solution is strictly analogous to that of molecules in space* (*Zeitschrift für Physikalische Chemie*, vol. i., Nos. 9 and 11).

Mason Science College,
October, 1889.

ATOMIC CONSIDERATIONS.

By Dr. T. L. PHIPSON, F.C.S., &c

The little monograph intitled "Outlines of a New Atomic Theory," of which I issued a fourth edition in 1886, has been distributed to many eminent chemists in Europe and America, and to some of the public libraries. Nevertheless, I desire to refer once more to the subject, as numerous letters that reach me still express objections, from which it appears that the writers have, to a certain extent, misunderstood my meaning.

I have endeavoured to show that *t is not the atom* which differs from one substance to another—it is not a different nature of atom which causes the difference between two bodies, but the *difference of space between the atoms*. An element is a system of atoms. Atoms are all alike in size, weight, and form. The space between the atoms, which I term *phlogiston*, implies movement, heat, and electricity. The element which has the most phlogiston is the most energetic. The elements which make up organic nature are the most energetic of atomic systems.

Surely this is simple enough: the theory in question proclaims the *unity of matter* by showing that the atoms of iron, sulphur, hydrogen, iodine, &c., are all of equal size and weight — in fact, identical—and that elements are systems of atoms, all identical.

I cannot here follow up this theory into its various ramifications and consequences, nor have I done so very elaborately in the original monograph; but if we admit the existence of atoms, as the most eminent chemical philosophers since the days of Dalton and Lavoisier have done, it appears to me that the above is the only rational conception of them. I must refer to my former paper for further considerations on this subject, and I trust that these few remarks will place my views in a clearer light to many correspondents who have endeavoured to raise objections to the theory.

London, December 2, 1889.

THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

(Concluded from p. 291).

The results of Mr. Bottomley's experiments were unfavourable. He found that the material had less susceptibility and more retentiveness than good soft iron, and that it had enormously less retentiveness than hard steel suitable for magnet-making.

Considerable attention having been given to the curious non-magnetic properties of manganese steel, the writer was led to make the approximate tests detailed in Table IV., to see if iron alloyed with other elements than manganese would also lose its magnetic susceptibility. From the list given it will be seen that practically manganese is the only exception; for, as regards ferro-chrome, it is only when very high percentages of chromium are reached that the material is not susceptible.

Malleable Ferro-alloys.—Malleable compounds of iron with other elements so far experimented upon (including carbon, silicon, sulphur, phosphorus, chromium, tungsten, aluminium, and nickel) are strongly susceptible to magnetisation.

Alloys of manganese and iron, however, form an exception to this. As is now well known in manganese steel, as soon as the manganese exceeds 8 or 9 per cent the material is only attracted when in a finely divided state, such as drillings or powder, and with further increase of manganese even this slight susceptibility disappears. The same fact is noticed as regards the non-malleable compounds of iron and manganese. Alloys of iron, nickel, and manganese are also not susceptible.

2. *Cast State.*—As might be expected, the whole of the samples are very free from honeycombs; but this soundness in the cast state is only acquired at the expense of toughness or ductility. As regards this freedom from honeycombs, it may be of interest to state here that although silicon does produce soundness in steel yet Mr. Holgate noticed that in making ferro-silicon of thirteen to fifteen per cent there is in casting an unusually large outburst of gas, and the pigs are exceedingly full of honeycombs. A sample is exhibited among the specimens accompanying this paper. In watching a cast of material of this percentage from the blast-furnace he noticed that when the exterior of the pigs became almost solid, and whilst the interior was still liquid, the metal began to boil up, and frequently for fifteen or twenty minutes some

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B Newcastle Meeting.

TABLE IV.—*Table of Ferro-alloys, Showing their Magnetic Susceptibility.*

Name of alloy.	Special constituent.	Composition per cent (in some cases approximate). C p.c.	Si p.c.	S p.c.	P p.c.	Mn p.c.	Cr p.c.	W p.c.	Al p.c.	Fe p.c.	Magnetic susceptibility. In bulk.	In drillings or powdered slate.
Spiegeleisen ..	Manganese.	4⅝	—	—	—	14	—	—	—	81¼	Attracted.	—
„ ..	„	5¼	—	—	—	36	—	—	—	58¾	Not attracted.	Very slightly influenced.
Ferro-manganese	„	7	—	—	—	82	—	—	—	11	„	Very slightly influenced.
Ferro-silicon ..	Silicon.	1	16	—	—	1	—	—	—	82	Strongly attracted.	—
„ ..	„	⅝	20	—	—	2	—	—	—	77½	„	—
Silicon-spiegel ..	Manganese and silicon.	2	8	—	—	20	—	—	—	70	Easily attracted.	—
„ ..	Manganese and silicon.	1½	16	—	—	20	—	—	—	62½	Strongly attracted.	—
Ferro-chrome ..	Chromium.	4	1	—	—	1	8	—	—	86	„	—
„ ..	„	5	2	—	—	1	28	—	—	64	„	—
„ ..	„	5	1	—	—	1	63	—	—	30	Not attracted in the slightest.	Very slightly influenced.
„ ..	„	5	2	—	—	1	79	—	—	13	Not attracted.	—
Ferro-aluminium	Aluminium.	1	1½	—	—	—	—	—	10	87½	Strongly attracted.	—
„	„	3	1⅛	—	—	—	—	—	12	83½	Very strongly attracted.	—
„	„	3	1⅛	—	—	—	—	—	18	77⅛	„	—
„	„	1	1⅛	—	—	—	—	—	20	77⅛	Slightly attracted.	Strongly attracted.
Ferro-tungsten..	Tungsten.	4	1	—	—	1	—	40	—	54	Very strongly attracted.	—
Ferro-phosphorus	Phosphorus.	1	⅛	—	10	4	—	—	—	84½	Strongly attracted.	—
Ferro-sulphur ..	Sulphur.	½	⅜	5	—	—	—	—	—	93¾	„	Strongly attracted.

TABLE V.—*Table of Corrosion Experiments.*

		Percentage of silicon.	Strength of acid.	Length of immersion.	Loss p. c.	Colour after treatment.	Remarks.
Silicon steel (C).. ..	Bar	1·60	50 per cent.	21 days.	6·32	Very bright.	After being taken out of the acid and dried, the silicon steel and wrought iron appeared as if burnished, and retained their brilliancy for some time.
„ (E).. ..	„	2·67	„	„	3·32	„	
„ (G).. ..	„	4·49	„	„	4·20	Very bright; soon dulled over, although carefully covered up.	
Ordinary mild steel ..	„	—	„	„	7·48	Dull bright.	
Wrought iron	„	—	„	„	4·47	Most brilliant.	
Silicon steel (E).. ..	Wire 20 B.W.G.	2·67	„	„	31·80	Very bright.	
Ordinary mild steel ..	„	—	„	„	17·29	Dull.	
Ordinary wrought iron	„	—	„	„	17·09	Very bright, like wrought bar.	
Manganese steel . ..	„	Mn 12%	„	„	51·18	—	

Moisture Test.

		Percentage of silicon.	Weight before placing in moist atmosphere.	Weight after keeping 21 days in moist atmosphere.	Increased n weight.
Silicon steel (C)	Bar	1·60	20·634 grms.	20·644 grms.	0·01 grm.

The following table gives the specific gravities of the silicon steel, also ferro-silicon :—

TABLE VI.—*Specific Gravities.*

		Percentage of silicon.	Specific gravity.	Remarks.
Silicon steel (E)	Ingot.	2·67	7·38	—
„ „	Wire 20 B.W.G.	2·67	7·88	—
„ „ (G)	Ingot.	4·49	7·54	—
Ferro-silicon	—	5·00	7·00	—
„ „	—	8·00	6·943	—
„ „	—	16·00	5·303	Doubtful.
Ordinary grey cast-iron . ..	—	—	7·10	—

cwts. of metal in each bed boiled over, this going on until the pigs were quite set and solid.

It would be interesting to know what is the cause of this outburst, and the composition of the escaping gases. It has been stated in metallurgical literature that in some hot overblown Bessemer charges silicon may be present in considerable percentages and yet the steel rise or boil over when poured into ingot-moulds.

Silicon steel pipes or settles to a much greater extent than ordinary steel, and this in itself is a considerable

disadvantage. Its fluidity when being poured is less than that of ordinary steel. The crystallisation or form of fracture of the lower percentages is somewhat like ordinary mild cast steel, but on exceeding about 2½ per cent Si a striking change occurs: the crystals become very large, glazed in appearance, and cleave somewhat after the nature of a spiegeleisen. As this large and marked crystallisation increases the material becomes exceedingly brittle, and if still further additions are made the appearance of the material approaches silicon pig-iron, and is non-malleable.

High percentages of silicon in the cast or unforged material cause a considerable increase in shrinkage or contraction. This point is already a difficult one with the steel-founder, who for many years has been on the horns of the dilemma that whilst silicon increases soundness it increases the tendency of castings to draw. In cast-iron this fact of silicon also increasing contraction has been noticed by Mr. Keep.

Also, as in the forged, so in the cast material, when the Si exceeds about two per cent and the peculiar crystallisation noticed in the samples exhibited commences, neither annealing nor water-quenching seems to have any effect in changing the structure.

It is well known that considerable difficulty is experienced in dissolving drillings of ferro-silicon; so tedious is the process that recourse is usually made to the sodium carbonate process. This is not requisite with silicon steel, which requires only the ordinary hydrochloric acid method. The silica residue is very clean and free from iron.

A considerable number of estimations have proved that the silicon is very uniform and homogeneous in this steel. Analyses taken from different parts of the same ingot and bar give results very similar to each other. No traces of graphite are noticed, the carbon always being present in the combined form. If the material analysed is in the form of drillings they keep their shape, the iron being dissolved out.

Experiments have been made with this steel in comparison with other material as regards its corrosion. The following table gives the time of immersion in the sulphuric acid, and the loss:—

Table VII.—*List of Samples Exhibited to Illustrate this Paper.*

Section I.—Samples of silicon steel in the cast state containing from 0·24 to 8·83 per cent of silicon.
Section II.—Samples of silicon steel in the forged state containing from 0·24 to 5·53 per cent of silicon.
Section III.—Test bars as mentioned in Table II.
Section IV.—Bending pieces given in Table II.
Section V.—Compression pieces given in Table III.
Section VI.—Samples of ferro-alloys to illustrate magnetic properties.
Section VII.—Silicon steel wire 2·67 per cent, 20 B.W.G.
Sample of ferro-silicon containing 16 per cent silicon, yet honeycombed.
Silica from silicon steel.
Also other samples.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick Graham Ansell, Wickwar, Gloucester; Sydney Hoare Collins, 19, Riverdale Road, Stoke Newington, N.; John B. Coppock, 126, Walton Street, Brompton, S.W.; Thomas Southall Dymond, 37, Hart Street, Bloomsbury; Cuthbert Chapman Gibbs, 3, Wyburn Villas, Surbiton; James Grant, Belmont Place, Chadderton, Oldham; Joseph H. Heywood, 23, Holland Street, Rochdale; James Guthrie, Mactaggart, Eskbank, Eltham, S.E.; James Sibun, 2, Lax Terrace, Norton, Stockton-on-Tees; Henry Wood Smith, B.Sc., Belmont, Higher Broughton, Manchester; John Stokes, Sarum House, Park Gate, Rotherham, Yorks; James Walker, 8, Windsor Terrace, Dundee; Sydney Russell Wells, 14, Girdlers Road, West Kensington.

The following were duly elected Fellows of the Society:— Messrs. Frank Thornton Addyman, Charles Frederic Baker, B.Sc., John Burgess, William Frederic Butcher, Frank Hill Perry Coste, David Brown Dott, Thomas William Dukes, Robert Stephen Edwards, B.A., James Kerr Erskine, John Simpson Ford, John Foggie, Harold Gripper, H. B. Helbing, Robert Edward Hughes, Eric Henry Jackson, James Robert Kaye, Henry Richard Kenwood, Frederick Thomas Knott, L. Napier Ledingham, G. B. Mason, James Braik Mason, Thomas Mercer, Joseph Alfred Nettleton, Wallace Christopher Nickels, J. T. Norman, James Gordon Parker, Alfred Edridge Pike, William Ping, Frederick Quincke, Ph.D., Sydney Steel, Sidney Augustus Sworn, John Bishop Tingle, Willis G. Tucker, M.D., Daniel Walker, B.Sc., William Whitehouse, Matthew Wittam, Basil P. Wigan, John Wiltshire, John Wilkie.

The following papers were read:—

102. "*Compounds of Phenanthraquinone with Metallic Salts.*" By Francis R. Japp, F.R.S., and Alfred E. Turner.

The authors have obtained several double compounds of phenanthraquinone with metallic salts, viz.,—

$$C_{14}H_8O_2 \cdot ZnCl_2,$$

which forms dark reddish brown needles, not melting even above 300°; $(C_{14}H_8O_2)_2HgCl_2$, crystallising in red, obliquely truncated prisms, melting at 222—223°; and $(C_{14}H_8O_2)_2HgCy_2$, which also forms red crystals, melting like the foregoing, at 222—223°. Oxysalts do not unite with phenanthraquinone.

They have prepared a similar compound (not analysed) from mercuric chloride and β-naphthaquinone; but could not obtain double compounds from benzoquinone, α-naphthaquinone, anthraquinone, diacetyl, and benzil. It would therefore appear that compounds of this class are derivable only from orthoquinones, and not from paraquinones, or open-chain α-diketones.

The intense colour of the double compounds in question indicates that in them the quinone preserves its distinctive character. In this respect they differ from the colourless compounds of the ortho-quinones with hydrogen sodium sulphite, the formation of which involves a reduction, and which are to be regarded as quinol-derivatives.

Discussion.

Dr. Armstrong remarked that the preparation and study of compounds such as the authors described were of importance in elucidating the nature of molecular compounds, and as affording valuable material for the discussion of the problem of valency. It was highly remarkable that the compounds were so much more intensely coloured than phenanthraquinone. Were their solutions equally coloured, and did the colour vary much with the concentration; would it not be possible by observation of the colour of solutions of varying strength to determine to what extent the compounds existed in solution, and at the same time to apply to them the Raoult freezing-point method?

Dr. Japp, in reply, said that the intense colour of the compound was at once apparent on mixing hot solutions of zinc chloride and of phenanthraquinone in glacial acetic acid, but the compound immediately begins to separate out; it was so sparingly soluble that it would not be possible to determine the molecular weight by

Raoult's method. In preparing the mercury compounds acetone was used as solvent; like the zinc compounds they were decomposed by water and also by acetic acid.

Mr. Chapman said that on mixing solutions of dextrose and of nickel oxide in ammonia, a dark green liquid was obtained of the colour of the compound, which subsequently crystallised out.

103. "*Action of Aldehyds and Ammonia on α-Diketones.*" By G. H. Wadsworth, Associate of Normal School of Science.

The author has studied the action of various aldehyds and ammonia on diacetyl, and has obtained the following glyoxalines:—

With benzaldehyd: *phenyldimethylglyoxaline*,—

$$C_{11}H_{12}N_2;$$

slender needles, melting at 230—234°.

With salicylaldehyd: *ρ-hydroxyphenyldimethylglyoxaline*, $C_{11}H_{12}N_2O$; satiny needles, melting at 218°.

With cinnamic aldehyd: *cinnamenyldimethylglyoxaline*, $C_{13}H_{14}N_2$; warty crystals, melting at 201—202°.

In addition, *cinnamenyldiphenyleneoxazole*, $C_{23}H_{15}NO$, has been prepared by the action of cinnamic aldehyd and ammonia on phenanthraquinone; slender yellow needles, melting at 171—172°.

104. "*Phenylhexamethylene Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

The authors find that on boiling phenyldehydrohexonecarboxylic acid,—

$$C_6H_5\cdot C{=\!=}C\cdot COOH \quad O< \quad >CH_2, \quad CH_2\cdot CH_2$$

with water it yields benzolybutyl alcohol,—

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

and carbon dioxide. This alcohol crystallises from water in large flat plates, which melt at 40—41°: although stable under ordinary conditions, when placed over sulphuric acid, the crystals rapidly disappear and are converted into oily drops of phenyldehydrohexone.

The *hydroxime*,—

$$C_6H_5\cdot C(N\cdot OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

is readily obtained by the interaction of benzoylbutyl alcohol, hydroxylamine hydrochloride, and excess of potash in alcoholic solution. It crystallises from benzene in colourless microscopic plates which melt at 56—57°.

Phenylpentylene glycol,—

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

prepared by the action of an excess of sodium amalgam on a dilute alcoholic solution of benzoylbutyl alcohol, crystallises from benzene in colourless concentrically-grouped needles, which melt at 54°; it is readily soluble in ether, alcohol, benzene, and hot water, but only sparingly in light petroleum.

Phenylpentylene dibromide,—

$$C_6H_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br,$$

is best prepared by dissolving the glycol in chloroform and gradually adding a slight excess of phosphorus pentabromide; it is a slightly brownish-coloured disagreeably-smelling oil, which is insoluble in water. It is readily acted upon by ethylic sodiomalonate, forming ethylic phenylhexamethylenedicarboxylate,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ \quad | \quad\quad | \\ CH_2\cdot CH_2\cdot C(CO_2Et)_2 \end{array}.$$

By heating the oily acid obtained from this ethereal salt at 180—200°, *phenylhexamethylene monocarboxylic acid*,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ \quad | \quad\quad | \\ CH_2\cdot CH_2\cdot CH\cdot COOH \end{array}$$

is produced. This acid is best purified by conversion, first into the barium salt and then into the crystalline ammonium salt. It crystallises from light petroleum in short thick prisms which melt at 104—105°; it is readily soluble in ether, alcohol, chloroform, and acetone, only moderately easily in cold light petroleum, difficultly soluble in water.

On boiling an alcoholic solution of phenylpentylene dibromide and ethylic sodacetoacetate the two substances readily interact, yielding ethylic acetylphenylhexamethylenecarboxylate,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ \quad | \quad\quad | \\ CH_2\cdot CH_2\cdot C(CO\cdot CH_3)\ COOC_2H_5 \end{array}.$$

On hydrolysis this ethereal salt yields phenylhexamethylenecarboxylic acid (m. p. 104—105°), identical with the acid described above, and *phenylhexamethylenemethylketone*,

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ \quad | \quad\quad | \\ CH_2\cdot CH_2\cdot CH\cdot CO\cdot CH_3 \end{array}.$$

This substance crystallises in colourless needles, melting at 78—79°, and distils at about 187—190° under 40 m.m. pressure without decomposition; the hydroxime produced by treating it with hydroxylamine and excess of potash in alcoholic solution is a thick colourless oil, which could not be obtained in a crystalline condition.

105. "*Diphenylfurfuran.*" By W. H. Perkin, Jun., Ph.D., and Aug. Schloesser, Ph.D., M.Sc.

Ethylic dibenzoylsuccinate,—

$$\begin{array}{l} C_6H_5\cdot CO\cdot CH\cdot CO_2Et \\ \quad | \\ C_6H_5\cdot CO\cdot CH\cdot CO_2Et \end{array},$$

is best prepared by treating an ethereal solution of ethylic benzoylacetate with the calculated quantity of sodium (1 atomic proportion) in the form of fine wire, and then adding a slight excess of iodine. It is converted by concentrated sulphuric acid into ethylic diphenylfurfurandicarboxylate,—

$$\begin{array}{l} C_6H_5\cdot C=C\cdot CO_2Et \\ \quad O< \quad | \\ C_6H_5\cdot C=C\cdot CO_2Et \end{array};$$

on hydrolysis it yields the dicarboxylic acid.

Diphenylfurfuranmonocarboxylic acid,—

$$\begin{array}{l} C_6H_5\cdot C=CH \\ \quad O< \quad | \\ C_6H_5\cdot C=C\cdot COOH \end{array},$$

is obtained, together with diphenylfurfuran, on heating the dicarboxylic acid to about 250°. It crystallises from benzene in short colourless needles which melt at about 214°. It does not yield a hydroxime when treated with hydroxylamine, neither is it affected by boiling with acetic anhydride.

Diphenylfurfuranmonocarboxylic acid tetrabromide, $C_{17}H_{12}Br_4O_3$, is produced when the finely-divided acid is exposed to the vapour of bromine as a hard crystalline mass, almost insoluble in solvents.

Diphenylfurfuran—

$$\begin{array}{l} C_6H_5\cdot C=CH \\ \quad O< \quad | \\ C_6H_5\cdot C=CH \end{array},$$

crystallises from light petroleum in pearly plates which melt at 81° and distil at a high temperature almost without decomposition. It is very readily soluble in benzene and alcohol, but sparingly soluble in cold light petroleum.

Diphenylfurfuran tetrabromide, $C_{16}H_{12}Br_4O$. This compound is readily produced when diphenylfurfuran is exposed for some hours to the action of bromine-vapour. The resulting dark-coloured mass becomes almost colourless when placed over caustic potash; when purified by re-crystallisation from benzene, it forms beautiful satiny plates melting at 190°.

Oktohydrodiphenylfurfuran, $C_{16}H_{20}O$, is produced when a boiling alcoholic solution of diphenylfurfuran is treated with an excess of sodium. It is a slightly yellowish-coloured oil which boils at 150—155° under 110 m.m. pressure.

PHYSICAL SOCIETY.

December 6, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MR. J. W. SWAN was elected a member of the Society.

The following communications were read:—

"*On the Electrification of a Steam-Jet.*" By SHELFORD BIDWELL, F.R.S.

The author showed that the opacity of steam issuing from a nozzle is greatly increased by bringing electrified points near it, and that its colour is changed to orange brown. Electrified balls and discs, when placed in the steam, produce similar effects, and when these are connected with an influence machine at work the decolouration of the jet rapidly responds to each spark. On examining the absorption-spectrum of the unelectrified jet, little or no selective absorption was detected, but, on electrification, the violet disappeared, the blue and green were diminished, and the orange and red remained unchanged. From these results the author concludes that electrification causes an increase in the size of the water particles in the steam, from something small compared with the wave-length of light, to about 1-50,000th of an inch in diameter. Allied phenomena with water-jets have been observed by Lord Rayleigh, who found that a straggling water-jet is rendered much more coherent by bringing a rubbed stick of sealing-wax near it.

These observations are of considerable meteorological interest, for the steam-jet phenomena go far towards explaining the cause of the intense darkness of thunder-clouds, and of the lurid yellow light with which that darkness is frequently tempered.

After making his experiments the author learnt that similar observations had recently been made by the late Robert Helmholtz, who viewed the steam-jets by reflected light against a dark background. On electrification the jets became much better defined, and presented diffraction colours. Luminous flames also produced similar effects, and Mr. Bidwell has found that glowing touch-paper is equally efficient. Helmholtz conjectures that the sudden condensation may be due to moleculur tremors or shock imparted by the electrification, upsetting the unstable equilibrium of the supersaturated vapour, just as a super-saturated saline solution is suddenly crystallised when disturbed. Another hypothesis suggests that condensation is caused by the introduction of solid matter into the jet by the exciting cause, thus providing nuclei upon which the vapour may condense.

On reading Helmholtz's paper the author tried the effect of gas-flames on water-jets, and found that, when luminous, they influenced the jet considerably, whereas non-luminous flames had no appreciable effect. He also found that luminous flames are positively electrified, and demonstrated this before the meeting.

Prof. RÜCKER thought the surface-tension of the films surrounding the water-jets might be lowered by the presence of a burning substance, and that the smoke from the touch-paper used in some of the experiments on steam-jets would introduce solid particles and facilitate condensation.

Mr. RICHARDSON enquired whether a red-hot iron had any effect.

Dr. FISON said he had made experiments on the electrification of flame, and found that potentials varying from +2 volts to −1½ volts could be obtained in the region within and surrounding a Bunsen flame.

Prof. S. P. THOMPSON commented on the contrast between Mr. Bidwell's experiments and those of Dr. Lodge on the dissipation of fogs by electricity, and also asked whether the colour of the jet depended on the length of spark produced by the machine.

Prof. FORBES thought a crucial test between the two hypotheses of Helmholtz could be obtained by trying the experiment in a germless globe.

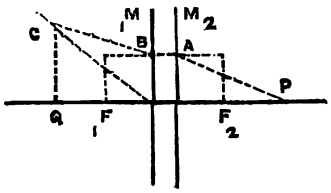
The PRESIDENT said he had recently noticed that gas-flames were electrified.

Mr. BIDWELL, in reply, said he ought to have mentioned that the effect of flames on jets may be due to dirt, for if soap or milk be added to the water in the steam-generator, no effect is produced by electrification or flame. As to change of colour with spark-length, little (if any) variation is caused thereby. He had not tried whether a red-hot iron produced any effect on a steam-jet.

"*Notes on Geometrical Optics: Part* II." By Prof. S. P. THOMPSON, D.Sc.

Three notes were presented, the first of which dealt with the geometrical use of "focal circles" in problems relating to lenses and mirrors, and to single refracting surfaces. By "focal circles" the author means the circles having the principal foci as centres, and whose radii are equal to the focal lengths. By their use the point conjugate to any point on the principal axis is readily determined. One construction for a mirror is to draw a tangent to the focal circle to a point, P, on the axis; the foot of the perpendicular to the axis, drawn through the point of contact, gives the point conjugate to P. When applied to a thin lens, a tangent is drawn, as above, to one focal circle, and the line joining the point of contact with the centre of the lens is produced to meet the other focal circle; a perpendicular to the axis from the remote point of intersection gives the conjugate point. Modifications applicable to thick lenses and single refracting surfaces were also given.

In his second note the author treated similar problems by the aid of squares drawn on the principal focal distances, the constructions being remarkably simple, as will be seen by the figure, in which M_1 M_2 represent the principal planes of a thick lens, F_1 F_2 its principal foci, and P and Q are conjugate points. The line B C is drawn parallel to P A.



In the third note the paths of rays through prisms are determined by the aid of imaginary planes representing the apparent position of the plane bisecting the dihedral angle of the prism when viewed through its two faces. Just as in problems on thick lenses in which the part between the principal planes may be supposed removed, so, when dealing with prisms, the part between the imaginary planes above referred to may be supposed non-existent. In another method of treatment the apparent positions of points outside the prism, when viewed from inside the prism, are made use of, and their application to illustrate dispersion was pointed out.

Mr. C. V. BOYS asked whether the latter construction could be used to show why the slit of a spectroscope appears curved.

"*On the Behaviour of Steel under Mechanical Stress.*" By Mr. C. H. CARUS-WILSON.

This was an enquiry into the properties of steel as illustrated by the *stress-strain* curves given in automatic diagrams from testing machines, and by magnetic changes which take place during testing.

After pointing out that the permanent elongation of a

bar under longitudinal stress consists of a sliding combined with an increase of volume, the author showed that the "yield" is caused by the limit of elastic resistance (ρ) parallel to one particular direction in the bar (generally at 45° to the axis), being less than along any other direction. When this lower limit is reached, sliding takes place in this direction until the hardening of the bar caused thereby raises the limit of elastic resistance in the direction referred to, to that of the rest of the bar, after which the stress must be increased to produce further permanent set.

From considerations based on the stress-strain curves of the same material when hardened to different degrees by heating and immersion, &c., it was concluded that the increase of (ρ) during "yield" is the same for all the specimens, and that the "yield" is a measure of the "hardness."

The question of discontinuity of the curves about the "yield point" was next discussed, and evidence to the contrary given by specimens which show conclusively that the yield does not take place simultaneously at all parts of the bar, but travels along the bar as a strain-wave. In these specimens the load had been removed before the wave had traversed the whole length, and the line between the strained and unstrained portions could be easily recognised. As additional evidence of continuity, the close analogy between the *stress-strain* curves of steel of various degrees of hardness, and the isothermals of condensible gases at different temperatures when near the point of liquefaction was pointed out; the apparent discontinuity in the latter probably being due to the change from gas to liquid taking place piecemeal throughout the substance (see Prof. J. Thomson, *Proc. Roy. Soc.*, lxxi., No. 130).

In seeking for an explanation of the hardening of steel by permanent strain, the author was led to believe this due to the displacement of the atoms within the molecules of the substance. To test this hypothesis, experiments on magnetisation by stretching a bar in a magnetic field were made; these show that the magnetisation increases with the stress up to the "yield point," and is wholly permanent when approaching that point. On comparing his results with Joule's experiments on the elongation of loaded wires produced by magnetisation, the author infers that there are two kinds of elongation; firstly, that produced by relative motion of the molecules; and secondly, an elongation resulting from a straining of the molecules themselves. To this latter straining the hardening by permanent strain is attributed, and this view seems compatible with the results of Osmond's researches on the hardening of steel.

Mr. F. C. Hawes's paper was postponed.

ROYAL INSTITUTION OF GREAT BRITAIN

General Monthly Meeting, Monday, December 2, 1889.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Messrs. Charles Vernon Boys, F.R.S., A.R.S.M.; Frederick Bayard Wiggins; and Alfred Fernandez Yarrow, M.Inst.C.E.

The Managers reported that they had re-appointed Professor James Dewar, M.A., F.R.S., as Fullerian Professor of Chemistry.

Electro-conductivity of the Eiffel Tower and its Earth Connections.—A. Terquem.—The totality of the lightning conductors of the Eiffel tower, fitted up according to the indications of MM. Becquerel, Berger, and Mascart, may be considered as very perfect and as likely to exert a protective influence over a considerable radius. —*Comptes Rendus*, Vol. cix., No. 23.

NOTICES OF BOOKS.

Ammonia and Ammonium Compounds: Comprising their Manufacture from Gas Liquor and from Spent Oxide (with the Recovery from the latter of the By-products, Sulphur, Sulphocyanides, Prussian Blue, &c.). Special Attention being given to the Analysis, Properties, and Treatment of the Raw Materials and Final Products. A Practical Manual for Manufacturers, Chemists, Gas-Engineers, and Drysalters. From Personal Experience, and Including the most Recent Discoveries and Improvements. By Dr. R. Arnold. Translated from the German by Harold G. Colman, Ph.D., M.Sc. London: Sampson Low, Marston, Searle, and Rivingtons.

This valuable work commences with the chemistry of ammonia. Here we find it declared, contrary to the recent results of M. Berthelot and other chemists, that plants have no power of absorbing atmospheric nitrogen. It is very desirable that this vexed question should come to a definite settlement. The author adds that probably "plants can only assimilate the nitrogen from nitric acid, and that the ammonia is first oxidised to that compound. This view is controverted by some recent researches of A. Muntz, which seem to show that ammonia can be utilised by plants as such.

In his account of the salts of ammonium, Dr. Arnold states that sal-ammoniac was originally known as *sal-armeniacum*, from having been brought into commerce by Armenian merchants. The name was subsequently changed to *sal-ammoniacum*, a name which had first been given to the sodium chloride found near the ruins of the Temple of Jupiter Ammon, in the Libyan Desert.

We find it said, on the authority of Woehler, that the deep black ink formed on mixing tincture of galls with ammonium meta-vanadate is not permanent.

For rapid estimations of ammonia the author recommends Knop's "azotometer," which is here described and figured.

In the second chapter, the author proceeds to the manufacture of ammoniacal salts. In speaking of the common method of determining the value of a gas liquor by the number of ozs. of pure sulphuric acid which it requires per gallon for saturation, Dr. Arnold reminds us that this test only indicates the amount of volatile ammonia. For determining the specific gravity he mentions, along with Twaddell's hydrometer, Fleischner's "densimeter." "In this instrument the specific gravity is obtained at once by putting the figure 1 and the decimal point before the number of degrees recorded." An instrument having this scale was in use in the Lancashire alkali district as far back as 1858. For a complete analysis of gas liquor the author gives the method of S. Dyson.

For the transport of sulphuric acid the author recommends iron tanks, in preference to the 17—20 gallon carboys employed in England. A 20 gallon carboy, especially in the case of so heavy a liquid as monohydrated sulphuric acid, is far too heavy to be manipulated with convenience and safety.

For obtaining ammonia from gas liquor, the continuous still of Feldmann is recommended.

After giving instructions for the analysis of ammonium sulphate, the author speaks of the competition between this salt and Chili saltpetre for manurial purposes. This circumstance has rendered the manufacture of ammonia much less profitable than it was until recently.

After describing the manufacture of the hydrochlorate, carbonate, and nitrate, Dr. Arnold passes to the sulphocyanide. The recovery of this salt from gas liquor has not been very widely practised, though R. Gasch thinks it ought to be more generally attempted, in preference to its manufacture from spent oxide.

The lime mud, and especially the waste liquor, from ammonia works are characterised as troublesome products

for which no satisfactory method of disposal has been elaborated.

The remainder of the work is devoted to the utilisation of spent oxide, and with appropriate tables. There is also a bibliography of the subject, and a list of patents, German and English, relating to the manufacture of ammonia and of its by-products.

The work must be pronounced thoroughly practical and calculated to be of great value to the interests concerned.

Facts and Observations concerning Railway Rates, and Practical Suggestions relating to the Classification of Merchandise Traffic by the Board of Trade. By J. W. Gray. London and Manchester: J. Heywood.

Mr. Gray argues that the railway companies, by training up in their goods offices thousands of young men in deceptive arts, are largely responsible for the corruption existing in the commercial world. He shows that, in spite of the recent Act of Parliament, the railways still carry alien manufactures and produce over their lines at lower rates than home traffic.

One of the remedies for such mischief the author does not mention: the enactment, as suggested by the late Peter Spence, of Manchester, that no railway company be permitted to own, lease, or work any canal or other channel of navigation.

Letts's Diaries for 1890. London, Paris, New York, and Melbourne: Cassell and Company (Limited), 1889.

These Diaries have been before the public for upwards of a century, and their convenience and variety have kept pace with the growing demands of the age.

The Rough Diaries, Nos. 31 and 48, interleaved with blotting-paper, the former giving three days to a page, and the latter half a page to a day, are perhaps the most useful kinds for the desk of the analytical chemist and man of science. The Blotting-pad Diary, foolscap size, is also very useful for the writing table. Among the smaller sizes may be mentioned the Office Diary, suitable for smaller memoranda and appointments, the Pocket Diaries, Nos. 26, 18, and 23 D, and the Medical Diary. The latter has proved to be so useful to medical men that we are tempted to ask whether it would not be worth the attention of the publishers to compile a similar pocket-book for chemists and physicists.

CORRESPONDENCE.

STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 293), H. N. D., Dublin, points out that "the use of ferrous ammonium sulphate for the preparation of standard iron solutions is not new." I beg to state that I did not claim it as such; I merely pointed out the use of H_2O_2 as the oxidising agent in preparing a pure ferric standard solution from the above salt, on account of the facility with which the excess of oxidising agent can be removed.

I should be extremely obliged if H. N. D. would point out the page and line in "Sutton," 1863, or any later edition, where the method is given.

I may state that I have not noticed this method given in any book, or should not have published it.—I am, &c.,

W. French.

Cambridge.

"NOTES ON QUALITATIVE ANALYSIS."

To the Editor of the Chemical News.

Sir,—Pardon my referring to your notice of my "Notes on Qualitative Analysis" (Chem. News, lx., 245).

I agree with you that "students who have not access to a well-stocked library" would certainly be unwise to attempt work with such a book; but with students such as we have here, and with the facilities for reference we possess, there is no possible doubt but that most excellent results are obtained by forcing a thorough examination of references, and then basing the daily interrogations upon those references. I go a step further in the attempt to make students think for themselves, by assigning them such cases from my private work as may come within the limits of their abilities. In such instances the student is brought into direct communication with the parties desiring the work done, and he writes and signs the final report. Such work being always done gratis, there is no difficulty in securing a sufficient supply.—I am, &c.,

William P. Mason.

Rensselaer Polytechnic Institute,
Department of Analytical Chemistry,
Troy, N.Y., December 4, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 23, December 2, 1889.

Formenic Fermentation of Farmyard Manure.—Th. Schlœsing.—During the formenic fermentation of farmyard manure at the temperature of 52°, no gaseous nitrogen is produced from a decomposition of nitrogenous compounds. There is no nitrogenous compound formed by the fixation of ammonia upon organic matter. On the contrary, nitrogen escapes from organic combinations and makes its appearance in the state of ammonia. The organic substance becomes impoverished in carbon more than in oxygen, whilst the proportion of hydrogen remains approximately the same. Water takes part in the decomposition of the organic substance, and supplies to the carbon at once oxygen and hydrogen. M. Berthelot made some remarks on the above paper from a thermochemical point of view, and called attention to the analogies between the formenic and the alcoholic fermentation.

Method of Measuring the Spherical and Chromatic Aberration of Object-Glasses for the Microscope.—C. J. A. Leroy.—In the present state of construction the problem of achromatism may be considered as solved, whilst this is far from being the case with aplanetism. The correction of spherical aberration requires, therefore, to be studied for the improvement of objectives.

New Researches on the Preparation and the Density of Fluorine.—Henri Moissan.—The apparatus now employed by the author is much longer than the one used at first. The U-tube of platinum in which the electrolysis is produced has a capacity of 160 c.c., and it can contain, during the preparation, about 100 c.c. of hydrofluoric acid. To prevent vapours of hydrofluoric acid from being carried over there is attached a small worm of platinum serving as a condenser, and kept in methyl chloride at about −50°. As hydrofluoric acid boils at 19·5°, almost all this compound is kept back in a liquid state at the bottom of the worm. After passing through the worm the gas traverses two platinum tubes filled with fragments of sodium fluoride. This compound energetically absorbs any hydrofluoric acid present. The

fluorine, thus purified, does not produce fumes in dry air, and it can be conveyed into the receivers by means of small flexible tubes of platinum. The specific gravity of pure fluorine has been determined as 1·26, which is very close upon the theoretical figure.

Certain Facts relative to the Analysis of Sugars.—E. Jungfleisch and L. Grimbert.—Weak acids do not modify the rotatory power of levulose, whilst the strong acids increase it to an important extent, though variable according to circumstances. This fact has a considerable influence upon the accuracy of the various methods used for the analysis of sugars. This is the case with the classical method of Clerget, in which the analysis of a mixture of saccharose and inverted sugar is effected with the polarimeter and by inversion. At the origin of this method Peligot and Dubrunfaut objected that it raised the weight of the saccharose. Experience has confirmed this opinion, and the authors detect a serious irregularity in the principle of the method.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 4.

The Determination of Extract in Wines by the Indirect Method.—E. Egger.—This memoir is not susceptible of reproduction.

Distinction of Fruit and Carrot "Kraut."—J. König and M. Wesener.—The substance known as "kraut" in Western Germany and "muss" in the East is a solution or extract of fruit, or of turnips, carrots, &c., evaporated down to a paste, and eaten upon bread. The article prepared from fruit, being much more valuable than that made from roots, is sometimes sophisticated with the latter. As "kraut" is not known in England, a reproduction of this memoir would have no interest for our readers.

Determination of Nitrogen by the Kjeldahl Method.—F. Martinotti.—The author's results seem to him to justify the following conclusions:—(1) For the determination of organic and ammoniacal nitrogen in manures in the absence of nitrates, the Kjeldahl method is preferable to that of Will-Varrentrapp, which has hitherto been in use. (2) For the determination of the total nitrogen in presence of nitrates, the Kjeldahl-Jodlbauer (see *Zeitschrift*, xxvi., 92) method is not suitable, as it does not give accurate results and requires too much time. It is better first to destroy the nitrates by heating with concentrated hydrochloric acid and ferrous chloride, and to determine them separately in another portion.

The Determination of Nitric Nitrogen by Kjeldahl's Method.—Dr. Otto Foerster.—This paper will be inserted in full as early as possible.

Purification of the Colouring-Matter of Litmus.—Dr. Otto Foerster.—Commercial litmus of the best quality is first extracted in the cold with common litmus, then digested with water, and the solution filtered and evaporated down. The residue is again dissolved in water, filtered, and the filtrate precipitated with absolute alcohol to which a little glacial acetic acid has been added. The precipitate is collected on a filter and washed with alcohol, when a violet fluorescent colouring-matter remains in solution. The residue is again dissolved in water, and the precipitation, filtration, and washing are repeated, when a red colouring-matter remains in solution, which, if dissolved in an alkali, appears violet. On a repetition of this process only a small quantity of colouring-matter remains in solution. The precipitate on the filter is dried and repeatedly moistened with alcohol to expel acetic acid. The precipitate is now again dissolved in water and the solution is filtered. The colouring-matter is finally precipitated with weak ammoniacal alcohol, collected on a filter, washed with pure alcohol, dried, and is ready for use.

A Contribution to the Determination of Ammonia by Distillation.—W. M. Stein and Paul W. Schwarz.

A New Apparatus for Titration.—Victor Hölbling.

Separation of Ethereal Solutions from Watery Liquids.—A. Gawalowski.—These three papers cannot be usefully reproduced without the accompanying cuts.

The Rise of the Zero-Point in Mercurial Thermometers made by Jena Normal Glass.—F. Allihn.—The glass in question contains:—

Zinc oxide	7
Calcium oxide..	7
Soda	14½
Alumina	2½
Boric acid..	2
Silica..	67
	100

Thermometers made of this glass showed an average depression of 0·05°; those of Thuringian glass, one of 0·4°; and those of English crystal glass (containing lead), 0·15°.

Gas-generating Apparatus with a Constant Efflux of Liquid.—Theodore Breyer.—This memoir requires the accompanying illustration.

On Horse-Fat.—Already inserted.

Quantitative Determination of Galactose.—E. Steiger.—This paper depends chiefly on the tables present.

Determination of Carbon in the Irons of Commerce.—L. Blum.—Already inserted.

Precipitation of Magnesia.—L. Blum.—Already inserted.

A Source of Error in the Separation of Small Quantities of Manganese from an Excess of Lime by Means of Ammonium Sulphide.—L. Blum.—Already inserted.

Wormwood Wine appears to be made by digesting wormwood in the local red wine.

Use of Kaolin Balls and of Salet's Pipette in Gas Analysis by Bunsen's Process.—N. Bunge (*Journal der Russisch Phys. Chem. Gesell*).—This paper requires the three accompanying figures.

A Collection of the Specific Gravities of Aqueous Solutions.—Dr. G. Th. Gerlach.—Nearly sixty pages of tables.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. vi., No. 3.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., Nos. 7 and 8.

Combustion-Heats of Isodibutylene and Isotributylene.—M. Malbot.

The Analysis of Methylanilines.—F. Reverdin and Ch. de la Harpe.—A criticism of a recent paper on this subject published by H. Giraud.

Determination of the Carbonic Acid of the Carbonates in Arable Soils.—J. A. Muller.—A volumetric process, executed with a modification of Scheibler's apparatus.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 23rd.—Medical, 8.30.
FRIDAY, 27th.—Quekett Club, 8.
SATURDAY, 28th.—Royal Institution, 3. "Electricity," by Professor A. W. Rücker, M.A., F.R.S.

THE CHEMICAL NEWS.

Vol. LX. No. 1570.

RESEARCHES ON THE CHEMISTRY OF THE CAMPHORIC ACIDS.*

By J. E. MARSH, B.A.,
Demonstrator of Organic Chemistry at the University Laboratory, Oxford.

For some time past I have been engaged in the study of some derivatives of camphor, with the view of determining, if possible, with some degree of certainty the constitution of that body. I do not propose to enter now into any account of the present state of our knowledge as to the chemistry of camphor, but at once to bring forward something of my own experience on this subject.

Of part of the results which I have obtained I gave a brief account at the meeting of the British Association last year at Bath. This account had reference chiefly to some further evidence of the relationship of camphor to hexahydrometaxylene, and to the products of oxidation of camphoric acid by means of an alkaline solution of potassium permanganate. These researches were not published, and are not even yet completed.

On the other hand, I have made some additional experiments which I am anxious to bring forward now, as it may be some time before the whole series is finished.

The experiments to be described have reference to certain processes which resulted in the preparation of a new camphoric acid; and the remarkable properties of this acid, contrasted with those of the ordinary camphoric acid, throw considerable light on the nature of the isomerism subsisting between these bodies.

Camphoryl Chloride.

I have had occasion to prepare considerable quantities of camphoryl chloride, $C_{10}H_{14}O_2Cl_2$, by the action of pentachloride of phosphorus on ordinary camphoric acid. Camphoryl chloride was obtained originally by Moitessier (*Comp. Rend.*, lii., 871), but only as a crude product, which he found to decompose on distillation. The substance may, however, be readily purified by distillation *in vacuo*, when it distils about 140° C. under 15 m.m. pressure. There appears to be no difference in the product of the reaction however much pentachloride of phosphorus is used, provided the temperature be not raised above that of boiling water.

Chlorocamphoryl Chloride.

If, however, camphoric acid is heated with a large excess of pentachloride of phosphorus on a sand-bath in a flask provided with a reflux condenser, a new body of the formula $C_{10}H_{13}Cl_3O_2$, viz., chlorocamphoryl chloride, is obtained. A further account of this body and its transformations I will reserve for a future publication.

The camphoryl chloride was prepared in order to attempt to reduce it to the lactone similar to the lactones obtainable from phthalyl and succinyl chlorides. It was not found possible to obtain a lactone under the various conditions of experiment from time to time adopted.

Action of Water on Camphoryl Chloride.

Circumstances, however, led to the consideration of a more simple reaction, namely, the action of water on camphoryl chloride. Moitessier had stated that this reaction was such as to give back camphoric acid. He means, presumably, the original dextro-rotatory acid, as he does not mention more than one. This acid is, in fact, formed, as will be shown subsequently, but only in very small quantity, and can only be separated from and recognised among the other products of the reaction after special treatment.

If camphoryl chloride obtained from ordinary dextro-camphoric acid is added gradually to about ten times its weight of hot water, there is formed about equal quantities of camphoric anhydride and a new camphoric acid, which rotates the ray of polarised light to the *left*. These two bodies are contained in the precipitate after cooling, and form by far the bulk of the product. Besides these, there is formed a small quantity of another substance more soluble in water, which separates from a strong hot aqueous solution as an oil, after a time solidifying. This is a mixture of the ordinary dextro-camphoric acid with the new lævo-rotatory acid. I will refer to this again later.

The camphoric anhydride and lævo-camphoric acid obtained in this reaction are readily separated by treatment with carbonate of soda in the cold, by means of which the lævo-acid is dissolved, leaving the anhydride untouched. This anhydride is converted into the ordinary dextro-rotatory camphoric acid by solution in hot caustic soda and precipitation by hydrochloric acid. I have been able to confirm de Montgolfier's observation that the camphoric acid obtained from the anhydride has a specific rotatory power of over +48°. I have found—

$$[\alpha]_D = +48{\cdot}25°.$$

(The determinations of rotatory power have been made throughout with a Laurent half-shade polarimeter, kindly lent me by Dr. Haldane, of the Physiological Department).

Properties of the Lævo-camphoric Acid.

The lævo-rotatory acid obtained above has a rotation about equal, and of opposite sign, to the dextro-acid. I have found $[\alpha]_D = -48{\cdot}09°$. I am convinced, however, that these two acids are not optically opposite isomers, in the sense namely in which dextro- and lævo-tartaric acids are regarded as optically opposite.

In its ordinary properties the lævo-acid differs markedly from the dextro-isomer. It has a lower melting-point, namely, 170° C., as compared with 185° C. Again it yields a very soluble amorphous barium salt, the corresponding salt of the dextro-acid being also indeed very soluble but crystalline. A more remarkable distinction, however, is that the lævo-acid appears to have no corresponding anhydride. When subjected to the action of acetyl chloride, an important reagent employed by Anschutz for obtaining the anhydrides of dibasic acids, the dextro-acid readily and practically quantitatively yields its anhydride, which is insoluble in carbonate of soda. The lævo-acid, on the other hand, when treated in the same manner, yields a product almost completely soluble in carbonate of soda, from which the original acid of melting-point 170° is recovered apparently unaltered.

Conversion of the Lævo- into the Dextro-Acid.

If, however, the lævo-acid be distilled, it boils about 294° C., yielding the anhydride of the ordinary dextro-camphoric acid, from which anhydride this acid may be obtained in the ordinary way.

Thus it appears possible to convert any quantity of the dextro-acid almost entirely into the lævo- through the intervention of the chloride, and any quantity of the lævo- back again to the dextro- by means of the anhydride.

Mixture of the two Acids.

Chautard obtained a lævo-camphoric acid by the oxidation of a lævo-rotatory camphor. This acid is described as possessing all the properties of ordinary camphoric acid, except that its rotatory power is of opposite sign. Further, when strong alcoholic solutions of the two acids are mixed, there is a precipitation of crystals and a rise of temperature in the liquid.

The lævo-acid which I have obtained differs from

* A Paper read before the Royal Society, December 5, 1889

Chautard's in other properties, and also in this, that when mixed with the dextro-acid in equal quantities in strong alcoholic solution there is no crystalline deposit and no rise of temperature.

On boiling down the alcoholic solution, a syrupy residue is left, which dissolves in hot water more readily, apparently, than either of its constituents. From the aqueous solution it separates partly as an oil, which after a time solidifies, and partly as crystals. Neither the solidified oil nor the crystals have a definite melting-point, but both melt at a lower temperature than either of the component acids. Hence the two acids do not appear to form any definite compound camphoric acid.

Separation of the Mixed Acids.

Anschutz's acetyl chloride reaction furnishes a particularly neat method of separating the two acids. The anhydride of the dextro-acid formed by the action of the acetyl chloride is separated from the apparently unaltered lævo-acid by treatment with carbonate of soda, which dissolves only the latter.

Nature of the more Soluble Syrupy Product of the Action of Water on Camphoryl Chloride.

This substance, which resembled the mixture of dextro- and lævo-acids above described, was subjected to the same process of separation, by which exactly the same products were obtained.

Thus the action of water on the acid chloride is such as to give about equal quantities of lævo-camphoric acid and the anhydride of dextro camphoric acid, a small portion of latter being further converted into the acid.

Optical Activity of Camphoryl Chloride and Camphoryl Anhydride.

It might be supposed, from the circumstances just mentioned, that camphoryl chloride which yields both dextro- and lævo-camphoric acids would be itself inactive. This, however, is not the case. I have always found camphoryl chloride to be lævo-rotatory, though I have not found a perfectly constant number to express its value. For the undiluted substance I have found $[\alpha]_D = -3{\cdot}0°$ and $-3{\cdot}6°$, while for the substance dissolved in crude benzene the rotation is about twice as much, viz. $[\alpha]_D = -7{\cdot}1°$ and $-8{\cdot}3°$; the latter value being obtained with the same specimen of camphoryl chloride which gave a rotation of 3·6° when undiluted. The rotation is, indeed, greater than that of camphoric anhydride, a substance which yields only one camphoric acid. I have found the specific rotation of camphoric anhydride in pure benzene to be $-3{\cdot}7°$, and very little different in the same benzene which was employed for the camphoryl chloride.

De Montgolfier has given a higher value, $-7°\ 7'$, for camphoric anhydride, which I am unable to confirm.

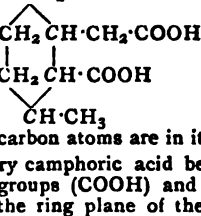
Theoretical Considerations.

If we wish to interpret rightly the foregoing facts, we shall, I think, find it impossible to regard the lævo-camphoric acid as the optically opposite isomer of the ordinary acid. On the other hand, there would appear to be a probability, almost amounting to certainty, that these two acids are related to one another as maleïc and fumaric acids, the dextro-camphoric acid corresponding to maleïc and the lævo- to fumaric acid. The isomerism is further complicated by the presence of rotatory power which requires the existence of two other isomers which shall be the optically opposite isomers of these two. In this latter case, therefore, the two acids will also be related, as maleïc and fumaric acid, but the lævo-acid will correspond to maleïc and the dextro- to fumaric. This lævo-camphoric acid is without doubt the acid which Chautard obtained by the oxidation of lævo-camphor, and the fumaroid dextro-acid I hope to obtain from it by the hydrolysis of the acid chloride.

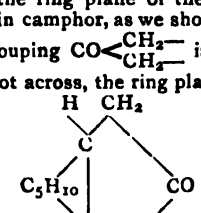
Now, accepting unreservedly Van't Hoff's carbon-atom hypothesis, we find that the isomerism of the camphoric acids is not explained by different structural formulæ, but ather by one and the same structural formula, admitting of at least four different arrangements of the atoms in space. There will be then two conditions attached to such a structural formula: (1) either it will contain two doubly-linked carbon atoms, each of them being united to two different groups, and one of these groups containing also an asymmetric carbon atom; (2) or the formula may consist of a closed chain of carbon atoms, of which two or more are asymmetric. In the latter case it is necessary to mention a further restriction, namely, that when there are only two asymmetric carbon atoms in the ring, there must not be symmetry in the formula, or, in other words, the image of neither isomer must be identical with its object (see *Phil. Mag.*, 1888, vol. xxvi., p. 426). It is the more necessary to mention this restriction as it applies to Wreden's formula, a formula which does not admit of rotatory power in the maleïnoid acid, that is, in the ordinary camphoric acid.

Turning now to some of the formulæ proposed for camphoric acid by different chemists, we find that in general they satisfy one or other of the conditions before mentioned. But Kekulé's formula, which fufils the first condition, and Kachler's, which satisfies the second, cannot be accepted, on the ground that they do not represent camphoric acid as a derivative of hexahydrometaxylene. Wreden's formula, which does thus represent camphoric acid, does not, as I have just mentioned, satisfy the restricted second condition. Armstrong's formulæ satisfy the second condition, and also represent camphoric acid as a derivative of hexahydrometaxylene; but Armstrong's formulæ appear to me liable to objection on the ground of the formula for camphor from which they are derived. These formulæ represent camphor either as not containing a ketonic group, or if it contains a ketonic group as containing also a closed chain of four carbon atoms. Now, we know no instances of stable rings of four carbon atoms, if indeed we know instances of such rings at all; and it is unlikely that camphor is the one exception to what may be regarded as a general rule.

The formulæ which I have proposed for camphor and camphoric acid appear to be opposed by no facts, and also explain perfectly the isomerism of the camphoric acids. Camphor is represented by the formula—

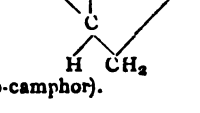


and camphoric acid by the formula—

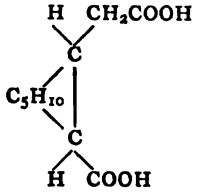


(The asymmetric carbon atoms are in italics).

Now the ordinary camphoric acid being the maleinoid acid has the two groups (COOH) and (CH_2·COOH) on the same side of the ring plane of the six carbon-atom nucleus. Hence in camphor, as we should naturally have supposed, the grouping $CO<\begin{matrix}CH_2—\\CH_2—\end{matrix}$ is also attached on one side of, and not across, the ring plane—

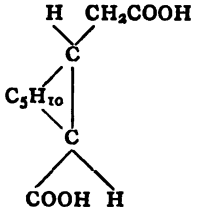


(dextro- and lævo-camphor).



(dextro- and lævo-ciscamphoric acid).

Again the lævo-fumaroid acid has the carboxyl and (CH_2COOH) groups on opposite sides of the ring plane.



(dextro- and lævo-transcamphoric acid).

On the other hand, Chautard's lævo-camphoric acid, being obtained directly from a lævo-camphor, will have the respective groups on the same side.

Nomenclature.

We may adopt the nomenclature introduced by von Baeyer to distinguish the hydroterephthalic acids. Ordinary camphoric acid, then, is dextro- and Chautard's acid lævo-ciscamphoric acid, the prefix *cis* indicating that the carboxylic groups are on the same side of the ring plane.

The new acid again, which I have described in this paper, is the lævo- and the acid yet to be discovered will be the dextro-transcamphoric acid, the prefix *trans* implying that the groups which govern the isomerism are on opposite sides of the ring plane.

It will be noticed that the formulæ which I have adopted require the existence of another series of two camphors (dextro- and lævo-) and four camphoric acids; but of the existence of these we have as yet no evidence.

Postscript, Dec. 2nd, 1889.—Since the above was written, my attention has been drawn to a paper by M. Friedel in the *Comptes Rendus* of last May, in which he describes a lævo-camphoric acid obtained from the substance known for some time as mesocamphoric acid. This lævo-acid appears to be the same as the one I have just described, and the mesocamphoric acid to be a mixture of the lævo- with the original dextro-acid. Thus mesocamphoric acid must no longer be regarded as a distinct isomer.

AN EASY METHOD OF DETECTING METALLIC SILVER IN THE PRESENCE OF LEAD.

By ALEXANDER JOHNSTONE, F.G.S. (Lond. and Paris), Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

As silver and lead very commonly occur in nature combined together in the same mineral substances, a more easy, rapid, and correct method for the detection of the former in the presence of the latter than any of those generally adopted in practice has for a long time been greatly desired, especially by assayers and mineralogists.

The author, who has spent much of his time in the determination of naturally occurring argentiferous lead compounds, has attempted to supply such a method in the extremely simple one detailed below, and he hopes it may prove, in the hands of others, as successful at it has invariably been with himself.

When a mineral which contains both of the above metals is heated in the ordinary course of blowpipe analysis, on charcoal with fusion mixture—

$$(K_2CO_3 + Na_2CO_3),$$

in the inner or reducing flame, it yields, as is well known, a malleable metallic lead (usually lead-grey in colour), which is an alloy of silver and lead. The silver is readily detected in this alloy* by treating it as follows:—Place it in an evaporating dish and cover it well over with moderately strong nitric acid, and then boil the liquid till the bead or beads dissolve; next nearly neutralise the solution thus obtained, with sodium carbonate, in a rough manner, but so that it will remain weakly acid after the operation. In this prepared solution now allow to lie for some time two strips—one of bright copper, and the other of zinc. The lead of the solution soon becomes deposited on the zinc, while the silver almost entirely goes to coat the copper foil; lift out the latter, and apply to the deposit on it a drop of fairly strong nitric acid, and then quickly afterwards a drop of potassium chromate solution. Or, dip the coated foil into moderately strong nitric acid for an instant, and then into a dish containing potassium chromate solution. The reddish brown mass which forms at once either on the upper or under side of the foil, is a sure indication of silver. The deposit on the zinc may be treated in the same way, and the lemon-yellow mass of lead chromate which results will contrast well with the brown incrustation obtained on the copper. If no silver is present in the solution the copper foil will scarcely become coated at all when placed in it.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, December 9th, 1889.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

With one exception only, the whole of the 182 samples examined were found to be clear, bright, and well filtered.

The condition of the water supply to the Metropolis during the month of November has continued satisfactory; but, with the coming on of winter, there was noticeable,

* Silver, it will be remembered, is, in almost every case, present only as a *minute* constituent in lead ores.

as had been anticipated in a previous report, a slight increase in the small proportion of organic matter recorded as present in the water for now several months past. Thus the mean proportion of organic carbon in the water distributed by the five companies taking their supply from the Thames, which amounted to 0·138 part in September and to 0·143 part in October, was found to be 0·153 part in 100,000 parts of the water in November, with a maximum of 0·178 part in any single sample examined during the month. It is noticeable, moreover, that the mean proportions of organic carbon present in the New River and East London Companies' supplies, though below the actual mean present in the Thames-derived supply, yet exhibited a somewhat greater relative increase during the past month.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

DETERMINATION OF WATER IN SILICATES, SUCH AS TOURMALINE, VESUVIAN, MICA, &c.

By P. JANNASCH.

The author has worked out a method for effecting this determination when ferrous and ferric oxides, boric acid, and fluorine may be present. The author takes account of the circumstance that such minerals lose their water at very high temperatures, and simultaneously lose such volatile compounds as silicon- boron- and iron-fluorides.

The author opens them up by heating an intimate mixture of the silicate with lead chromate. Lead silicate is formed and all the water is set at liberty, whilst the halogens or other acid groups present remain in combination with the lead.

He uses thin tubes of potash glass of about 10—12 m.m. diameter within, and gives them the shape of a short combustion-tube of 46 to 47 c.m. in length. The previous ignition of the chromate, the drying, and filling the tube are effected in the manner usual in ultimate analysis.

The arrangement of the tube is as follows :—A current of air is introduced into a vacant space of about 4 c.m. at the end. Then follow copper turnings, 1 c.m.; granulated chromate, 10 c.m.; fine chromate, 1·5 c.m.; a mixture containing the substance, 6·5 to 7 c.m.; fine chromate, 5 c.m.; granulated chromate, 18 c.m.; copper turnings 1 to 2 c.m. Next follows an open space and then the perforated stopper.

The finely powdered mineral, dried previously for an hour over calcium chloride, must be intimately mixed with an excess of very finely ground chromate, so that the stratum of the mixture may take up a length of 6·5 to 7 c.m. in the tube. After the tube has been fully charged, and knocked so as to leave an air-channel, it is laid in a short combustion-furnace with about 20 round burners giving high flames. Before the calcium chloride tube is laid a soda-lime tube of the same shape, and in front of this a small U-shaped safety tube with fragments of potassa. The drawn-out end of the combustion-tube is then connected with a good drying system (potassa-lye, sulphuric acid, potassa in fragments, and granulated calcium chloride) and an air-gasholder. A slow current of anhydrous air—about 100 bubbles in a minute—is drawn through the apparatus and the heating is then begun and conducted much in the same manner as in a combustion. After the first layer is at full redness almost up to the substance and the end also, the remaining burners are opened almost simultaneously. The layer with the substance must be ignited as strongly as possible, as also the adjacent chromate, until it enters into fusion. After this heat has been attained it must be kept up for at least fifteen to thirty minutes, as strongly as possible.

Whilst the chief mass of the water collects in the calcium chloride tube the current of air is accelerated to about 150 bubbles per minute, though it is afterwards slackened again to the original rate. Both the drawn-out point and the front of the combustion-tube must project well out of the furnace. A movable screen at the front of the furnace is necessary. The foremost tile on the left of the current of air is omitted, and, where the substance lies, a tile is laid over the furnace. All the other tiles are placed close to each other. When the operation is complete the apparatus is not weighed before the lapse of an hour.—*Berichte Deutsch. Chem. Gesell.* and *Zeit. für Anal. Chemie.*

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID BY MEANS OF MOLYBDIC ACID.

By A. GRETE.

In the analysis of bone-dust in which the organic substance had not been entirely destroyed, the author observed that, after the addition of the first drops of the molybdic solution, there appeared a white flocky precipitate, which, on the further addition of the solution, seemed to become transformed into the ordinary yellow precipitate. The suspicion that the white precipitate was occasioned by the presence of gelatin was confirmed, as it was found possible to throw down all the phosphoric acid from a solution, on the addition of a sufficiency of glue, in the form of a flocculent precipitate, which, in more concentrated solutions, appears curdy. But all attempts failed to obtain, in this manner, in the cold, precipitates of a constant composition. The more glue was present, more was evidently taken up in the precipitate. In heat, also, the appearance of the precipitate varied according to the quantities of glue.

The author utilises these reactions as follows:—

A measured quantity of a solution containing phosphoric acid is neutralised in a beaker, using methyl orange as indicator, and any slight turbidity is re-dissolved by a few drops of nitric acid. There is then added about an equal volume of a 75 per cent solution of ammonium nitrate, and about 1 grm. sodium sulphate and 1 c.c. of a solution of glue, heating to 80°—90°. The liquid thus prepared is directly titrated with a molybdic solution (prepared as below), agitating frequently until the clear liquid, after the addition of a drop, no longer shows any precipitation in the form of a dark cloud. The thick white precipitate produced at the beginning of the titration gradually becomes yellower and more curdy, so that further precipitations, which are white at first, show distinctly against this background. After shaking up the liquid it is tested again, adding, from time to time, small portions of glue as long as this alone produces any turbidity, and the approaching end of the operation is recognised by the decreasing strength of the reaction. When a precipitation can no longer be recognised on a drop of the standard molybdic liquid falling into the phosphoric solution, and when a solution of glue no logner produces a white turbidity, the whole (which should have been kept as hot as possible) is heated, whilst stirring, until the curdy precipitate becomes finely granular. In the clear liquid, especially if viewed from the side, the slightest turbidity occasioned by the further addition of a drop of the molybdic solution can be distinguished, and the liquid can then again be rendered clear by shaking.

If too much molybdic acid solution has been inadvertently added the error may be corrected by the introduction of a known number of c.c. of a solution of phosphoric acid and again bringing on the final reaction.

The presence of ammonium nitrate in increasing proportions depresses the results, which, however, can be kept constant if the above proportions are retained. On the other hand, sulphates slightly raise the results Varying quantities of acid act in the same manner, and should therefore be neutralised. But the acid which is introduced along with the molybdic solution does not interfere with the constancy of the results. Small quantities of chlorides have no appreciable influence upon the result.

The necessary solutions are prepared as follows:—

1. Molybdic acid solution:—1 kilo. ammonium molybdate dissolved in ammoniacal water and 100 grms. gelatin boiled for some time with water and a little nitric acid are mixed together, and the faintly alkaline yellow liquid is poured into about 3 litres of nitric acid of sp. gr. 1·2. The mixture is made up to 10 litres and kept for several days with frequent shaking. A flocculent phosphatic solution is soon deposited, after the removal of which the solution is perfectly clear and permanent, whilst without gelatin yellow deposits separate out.

2. Solution of ammonium nitrate at 75 per cent, containing about 40 grms. sodium sulphate per litre.

3. Solution of gelatin:—100 grms. gelatin are boiled in water and 50 c.c. nitric acid and made up to 1 litre. A few c.c. of this solution suffice for precipitating 0·1 grm. P_2O_5. If the gelatin solution contains phosphoric acid—which frequently happens—it must first be removed.—*Zeitschrift für Analyt. Chemie* and *Berichte Deutsch. Chem. Gesells.*

ON THE TANNIN IN INDIAN AND CEYLON TEAS.

By DAVID HOOPER, F.C.S., F.I.C.

The proximate constituents of tea leaves have been studied and estimated by various chemists with equally varying results and conclusions. The alkaloid therein, physiologically the stimulating principle of tea, has been determined in various samples, but the results have shown that no relation exists between the amount present and the commercial value of the leaf, or the elevation at which the bushes grow. A number of elaborate analyses have been published on the composition of the inorganic matter or ash of tea, but it seems that no useful lessons to the planters can be drawn from these tables.

The tannin of tea has also been investigated, both qualitatively and quantitatively, but as the subject has been treated by so many experts, using different methods, and applying them to different samples, the results are not comparable, and leave the subject open for further enquiry.

Mulder's analyses of tannin in teas are often quoted in text-books; his figures for black tea are 12·88, and green tea 17·80 per cent; Dragendorff found in teas of Russian commerce 9·42 to 12·70 per cent; Jank obtained a maximum of 9·14, and a minimum of 6·92 per cent in eighteen samples; Wigner, analysing some astringent teas, reported as much as 27·7 to 42·3 per cent; Hassell gives as the average 15·24 in black, and 18·69 per cent in green teas; Clark found from 5 to 19 per cent; and Geisler, an American chemist, obtained 14·87 as the average percentage of tannin in a large number of packages of Indian teas imported into New York.

The interpretation of these figures has been also remarkable. Some isolated analyses have recently gone the round of the Indian papers, to the effect that an Indian tea gave 9·68 per cent of tannin, and a Chinese tea 6·01 per cent, and these figures have been quoted with a view to disparage Indian teas, and to exalt the virtues of Chinese leaves. The teas of Ceylon have also been examined, and from a few analyses it has gone forth that the tannin, as a rule, in the teas of this island

	Description of sample.	Elevation.	Tannin Per cent
	Nilgiris—		
1.	Dodabelta, Orange Pekoe ..	7800	13·55
2.	,, Pekoe	,,	13·23
3.	,, Souchong	,,	12·32
4.	,, Congou	,,	11·08
5.	Green leaves, inferior	7000	19·19
6.	,, Liddellsdale ..	6500	16·38
7.	,, Young bushes ..	,,	19·00
8.	,, Hybrid	6000	18·66
9.	,, China variety ..	,,	16·62
10.	,, Assam hybrid ..	3100	21·03
11.	,, Coarse..	,,	11·52
12.	Hope Estates, Orange tips ..	4000	18·61
13.	,, Orange Pekoe ..	,,	18·35
14.	,, Broken Pekoe ..	,,	17·52
15.	,, Pekoe	,,	16·85
16.	,, Pekoe Souchong	,,	17·53
17.	,, Souchong	,,	15·88
18.	,, Congou	,,	13·19
19.	,, Tray dust.. ..	,,	18·55
20.	,, Bulk tea	,,	18·00
21.	,, Green Mandarin broken	,,	24·37
22.	,, Green ,, Pekoe	,,	23·85
23.	,, Green Bulk	,,	23·50
24.	Aratapara, Orange Pekoe.. ..	3400	14·48
25.	,, Pekoe	,,	14·14
26.	,, Pekoe Souchong ..	,,	12·25
27.	,, Souchong..	,,	11·96
28.	,, Congou	,,	10·14
29.	,, Dust..	,,	14·42
	Travancore—		
30.	Seafield, Broken Pekoe	2500	19·95
31.	,, ,, ,, ...	,,	21·22
32.	,, Pekoe Souchong ..	,,	20·90
33.	,, ,, ,, ...	,,	21·13
34.	Poonmuddi, Broken Pekoe ..	2600	17·45
35.	,, Pekoe	,,	17·37
	Coorg—		
36.	Munza-collie, Orange Pekoe ..	4000	16·93
37.	,, Pekoe	,,	16·32
38.	,, Souchong	,,	15·15
	Ceylon—		
39.	Glenorchy, Broken Pekoe ..	5700	19·00
40.	,, Pekoe	,,	17·90
41.	Brownlow, Broken Pekoe.. ..	4000	20·80
42.	,, Pekoe	,,	19·22
43.	Ancombra, Broken Pekoe.. ..	2500	18·40
44.	Yellangowry, Pekoe	,,	15·67
45.	,, Pekoe Souchong .	,,	15·00
46.	Bandarapolla, Broken Pekoe ..	1600	18·53
47.	,, Pekoe..	,,	17·40
48.	,, Pekoe Souchong	,,	17·20
49.	Kanangama, Broken Pekoe ..	200	20·87
50.	,, Pekoe	,,	17·48
51.	,, Pekoe Souchong .	,,	15·41
	Assam—		
52.	Orange Pekoe	600	20·80
53.	Pekoe	,,	20·43
54.	,, ...	,,	18·68
55.	,, ...	,,	19·25
56.	Broken Pekoe Souchong.. ..	,,	16·83
57.	Pekoe Souchong	,,	16·18
	Darjeeling—		
58.	Orange Pekoe	3000	13·61
59.	Broken Pekoe	,,	17·74
60.	Pekoe	,,	16·37
61.	,, ...	,,	13·67
62.	Pekoe Souchong..	,,	14·74
63.	,, ,, ...	,,	14·64
64.	,, ,, ...	,,	14·52
65.	Fannings	,,	15·25

is much smaller than in Indian specimens. Again, tea growers on the mountain tops have used figures to show the superiority of their produce compared with that of the plains, and the following extract taken from a local paper, circulating in a planting community, will show what ignorance is displayed on the subject:—

"The strong rasping Assam brew, and the make of all gardens situated at low elevations, are known to contain upwards of 75 per cent of tannin, while mountain trees are comparatively free from this deleterious ingredient."

The tannin of tea leaves, according to Rochleder, Hlasiwetz, and Malin, is allied to quercitannic acid, and according to Kellner is identical with gallotannic acid. It is precipitated from its solution with acetate of lead, forms an insoluble precipitate with gelatin, and inky mixtures with salts of iron; it is associated with gallic acid, boheic acid, oxalic acid, and quercetin, and is the source of the astringency of the tea. From the numerous methods for the estimation of tannin, the one that commended itself to me was the use of a solution of acetate of lead to a filtered decoction containing by exhaustive boiling the soluble constituents of the leaves. The process is simple, and it was found to give most concordant results when working on the same sample. The lead precipitate would contain some of the gallic acid and the oxalic acid, if any were present, and therefore the weight of this precipitate was an excellent gauge of the astringent properties present; the dried precipitates were found to have a composition averaging 50 per cent of plumbic oxide, a result agreeing with the constitution of gallotannic acid. The value of the present investigation consists in the observance of the minutest detail in the process being carried out under exactly similar conditions, although applied to different samples. The teas were all air dried, and contained from 5 to 6 per cent of moisture, the green leaves were dried in a water-oven previous to analysis, and the results were calculated upon the leaves containing 5 per cent of moisture.

It will be observed in the above Table that the finest teas are those which contain the most tannin, and there is a gradual declension of this principle as we approach the Souchong and congous. The elevation does not appear to affect the amount of tannin as has been supposed. The Dodabelta Estate, the highest in the list, shows a smaller percentage of tannin in the leaf than all the rest, but does not very much differ from the samples from Aratapara, some 4400 feet below; and in this respect there is very little to learn from the altitudes of the Ceylon teas. The highest tannin content occurs in Travancore tea of Seafield Estate, a tea of great fragrance, and considered to rank very high-class in the home market, and the Glenorchy Broken Pekoe of Ceylon, although containing 19 per cent of tannin, is one of the best priced teas of the island. The determination of Nos. 9 and 10 shows that the kind of shrub cultivated in India contains more or less tannin according to its original habitat. The coarse leaves, No. 11, were taken from the lower part of the bush, and were such as are never made use of in the factory. The green teas are very astringent, and, as they are made from the same estate as those above, it is evident that some of the astringency is rendered insoluble in the process of manufacture.

The amounts of tannin shown in the list, it must be remembered, are obtained by perfectly exhausting the leaves, and do not represent the amount taken in domestic use. The infusion of the family tea-pot extracts more or less tannin, according to the sample used and the time allowed for the leaves to soak in the boiling water. The brokers' test of five minutes takes out one-fifth of the extract, with a corresponding amount of tannin. The tea-pot infusion of ten minutes removes about one-third, fifteen minutes one-half, and twenty minutes two-thirds. The following experiments were made to show the amount extracted by infusing 1 per cent of tea in boiling water for five and fifteen minutes:—

	Tannin. Per cent.	Extracted in five minutes. Per cent.	Extracted in fifteen minutes. Per cent.	
A. ..	11·08	3·04	27·4	—	—
B. ..	12·10	4·40	36·2	6·88	56·8
C. ..	12·32	4·28	34·7	—	—
D. ..	13·25	—	—	7·88	59·5
E. ..	13·55	4·60	33·9	—	—
F. ..	23·50	6·26	26·6	9·52	40·0

The tannin is, undoubtedly, the source of the "strength" of the tea, and the higher the tannin the richer the infusion, and the more of body will the sample possess. Tannin is likewise a natural constituent of the tea, and is not amenable to suppression by higher cultivation, or by the ordinary processes of manufacture. The excellent qualities of Indian teas are accompanied by a high percentage of this substance, and therefore must be treated as strong teas, either by diluting them with weaker Chinese, or by taking a much smaller quantity when required for infusion in the tea-pot. If a smaller amount of these strong teas is taken, if good water is used for the infusion, if it is allowed to stand not longer than ten minutes, we should not hear so much of the "deleterious ingredient" in this universally used beverage.

Ootacamund, India.

THE MAGNETISM OF NICKEL AND TUNGSTEN ALLOYS.*

By JOHN TROWBRIDGE and SAMUEL SHELDON.

Introductory.

The fact that different kinds of steel, alloyed in small proportions with tungsten or wolfram, and magnetised to saturation, increases in specific magnetism,† has long been known. Whether the same effect would result from the use of nickel alloyed with tungsten has never been investigated. This paper has for its object a partial answer to the query. It was instigated by Mr. Wharton, proprietor of the American Nickel Works, whose chemist, Mr. Riddle, kindly prepared the alloys which have been employed. These alloys were in two groups. The first, received in November, 1888, consisted of three bars of the same shape, one being of pure nickel and the other two having respectively 3 and 4 per cent of tungsten in alloy. These bars were rolled from cast ingots, which were toughened by the addition of magnesium after Fleitmann's method, the magnesium being added just before pouring. They were hot when rolled. The one of pure nickel was afterwards planed into regular shape. Those containing tungsten were too brittle to allow of this manipulation. They were, however, of sufficient regularity to permit accurate measurements. This group contained also an octagonally-shaped bar with 8 per cent of tungsten, which was prepared like the others, and was afterwards ground into shape.

The second group, received in May, 1889, contained bars which were simple castings, made without the addition of magnesium, and consisted of pure nickel and alloys with 1, 2, 3, and 6 per cent of tungsten. All the bars in this group were extremely hard and brittle. In making them, tungsten oxide, of weight calculated to yield the desired percentage of tungsten in the resulting alloy, was placed with adequate carbon in the bottom of a graphite crucible and covered by the proper weight of pure grain nickel. All was then covered with borax, the lid of the crucible was placed on, and the crucible was heated until reduction and fusion were completed.

* From the *Proceedings of the American Academy of Arts and Sciences.*

† *Journ. Chem. Soc.*, 1868, xxi., 284, says 300 per cent

Method.

As the suspected influence of the tungsten would be to affect the magnetic moment of the bars, these were magnetised to saturation and their specific magnetism then determined, *i.e.*, the magnetic moment for each grm. of metal.

The magnetisation was effected by placing the bars separately in a hollow coil whose length was 15 c.m. and outside and inside diameters respectively 6 and 3 c.m. It consisted of six layers of wire having 63 turns each. A dynamo current of 40 ampères was then sent through the coil for one minute, and the circuit then broken and the bars removed.

For the determination of the magnetic moment, use was made of a reflecting magnetometer, and deflections were observed with a telescope and scale at a scale-distance of 100 c.m. Measurements of the horizontal intensity, H, of the earth's magnetism were first made. The results from these determinations by means of the first and second Gauss arrangements were, respectively,—

$$H = 0{\cdot}1724 \text{ c.m. g. s.}$$
$$H = 0{\cdot}1720 \quad ,,$$

The freshly magnetised bars were then placed in the second Gauss position relative to the magnetometer, and the angular deflection determined. The specific magnetism, S, was then calculated by the formula—

$$S = \frac{r^3 H \tan \phi}{m},$$

where—

r = Distance from bar to magnetometer = 72·68 c.m.
H = Earth's horizontal intensity = 0·1722.
m = Mass of the bar.
ϕ = Angular deflection of magnetometer.

Results.

The mean results of two sets of observations on Group I., and also upon a similar bar of soft tool steel, are given in the following Table :—

Group I.

Composition.	Size in c.ms.	Mass in grms.	S[c.m.$\frac{3}{2}$ g.$-\frac{1}{2}$ sec.-1]
Pure nickel	18×2·7×0·65	284·5	1·23
Ni+3 p.c. W	,, ,, ,,	286·5	10·60
Ni+4 ,, W	,, ,, ,,	283·5	10·40
Tool steel	15×2·5×0·5	159·5	7·46
Ni+8 p.c. W	(13×1·5) (octagonal)	144·0	5·25

roup II., of cast bars, gave the following results :—

Group II.

Composition.	Size in c.ms.	Mass in grms.	S[c.m.$\frac{3}{2}$ g.$-\frac{1}{2}$ sec.-1].
Pure nickel	18×1·8×1·6	459	1·05
Ni+1 p.c. W	,, ,, ,,	455	1·92
Ni+2 ,, W	,, ,, ,,	454	1·70
Ni+3 ,, W	,, ,, ,,	463	1·75
Ni+6 ,, W	,, ,, ,,	465	1·15

The bars of both groups were, subsequent to the above observations, completely demagnetised and then freshly magnetised. New determinations gave the same results as before. The demagnetisation was accomplished by placing the bars inside two coils, which were traversed by currents from an alternating dynamo. The coils were then slowly drawn apart, and the bars maintained at a position central between them. After treatment in this manner, they showed no appreciable deflection when placed in position relative to the magnetometer.

The results tabulated indicate that tungsten greatly increases the magnetic moment of nickel, if the alloy be forged and rolled, but, on the other hand, has but small influence if they be simply cast. Furthermore, changes in the amount of tungsten do not appear to cause corresponding changes in the magnetic properties.

To see whether the remarkable effect in bars 2 and 3, as compared with bar 1, of Group I., was owing to some molecular condition of their surfaces induced by rolling, two bars from the same steel, one rolled and the other pressed, were magnetised and then measured. The ratio of the specific magnetism of pressed to rolled was 9 to 5, the rolled having the smaller amount. The existing difference, in this case, is probably owing to a difference in hardness, rather than to any molecular condition of the surfaces.

The specific magnetisms of all the bars are small when compared with good steel magnets. Kohlrausch says that good magnets, of common form, should have S=40. The bar of ordinary tool steel, however, retained but 7·46. Still it was soft, and by tempering would doubtless have doubled this value.

If forged, nickel and tungsten can be made to maintain a specific magnetism of 10; it will form a useful addition to the resources of physical laboratories. From the high polish of which it is susceptible and its freedom from damaging atmospheric influences, it will be most happily suited for the manufacture of mirror magnets where magnetic damping is to be employed.

CONTRIBUTION TO THE KNOWLEDGE OF BORON.*

By HENRY C. C. MAISCH, Ph.G., Ph.D.

During his researches on the electrolysis of the alkaline oxides and hydroxides, Sir H. Davy also subjected boric acid to the action of the electric current (*Phil. Trans. Royal Society*, 1808, p. 43). He obtained a black combustible substance, which, however, he did not further describe. Without doubt he was the first to obtain boron in the free state, though to two French chemists, Gay-Lussac and Thénard (*Gilb. Ann. der Phys.*, 1808, p. 30), belongs the credit of first describing the element, which they obtained by the action of potassium on melted boric acid. During the year 1888, W. Hampe (*Chem. Zeit.*, xii., 841) prepared boron by the electrolysis of borax, which he melted in a graphite crucible.

Wöhler and Deville (*Ann. Chim. Phys.*, 1858 (3), lii., p. 84) during their classic researches on boron and its compounds, employed the process of Gay-Lussac and Thénard, using potassium or sodium, but they also found that, by using aluminium, crystalline boron was obtained.

We are indebted to Berzelius for two further methods: (1) by the action of potassium on boron fluoride, and (2) by the action of potassium borofluoride at the fusing-point of the former. Wohler and Deville (*loc. cit.*) and Geuther (*Jenaische Zeitschr. fur Med. und Naturw.*, ii., p. 209) found that, in place of potassium or sodium, magnesium could be used to advantage in the last method.

On the advice of Prof. L. Gattermann I took up the reduction by means of magnesium, using, in place of potassium borofluoride, the cheaper borax. This was employed in the form of powdered borax glass, because the water of crystallisation otherwise present would have an injurious effect on the reaction.

Without going into details as to the experiments made with the idea of finding the best proportion of the reagents to be used, I will simply give the one which was found to be the best. The bottom of a Hessian crucible was covered with the powdered borax glass; on this an intimate mixture of two parts borax and one part magnesium powder was packed, so as to drive out as much air as possible, and this was covered by about half an inch of powdered borax glass, which is to fill the crucible. The lid is then fastened down with moist clay, and the whole

* *Am. Journ. Pharm.*, December, 1889.

subjected to the heat of a well drawing charcoal furnace, the crucible being surrounded by the fuel, which is allowed to burn down once. After cooling, the crucible is broken and the product finely pulverised. The powder is extracted with, boiling water, and, after cooling, thrown in small portions into cooled diluted hydrochloric acid and allowed to remain for four or five hours, after which it is filtered off and subjected to the action of concentrated hydrochloric acid for about two hours. The powder is then filtered off, washed with water, and dried either by the heat of a water-bath or by the following method:—The water is replaced with alcohol, this in turn by ether, and this allowed to evaporate at the temperature of the room. The boron thus obtained is by no means pure, but answers perfectly well for the preparation of its halogen derivatives.

Boron Trichloride.—The first method to be found in literature is that of Berzelius (*Pogg. Ann.*, 1824, ii., p. 147), who states that amorphous boron which has been dried in a vacuum ignites in an atmosphere of chlorine at ordinary temperatures, while boron which has been heated reacts only at higher temperatures. Some decades later Wöhler and Deville (*loc. cit.*) showed that the same takes place in hydrochloric acid gas; the reaction, however, must be completed at higher temperatures. They also found that by the action of boron on mercuric chloride, lead chloride, or silver chloride, this compound was likewise obtained.

The method which has been used up to the present for the preparation of the chloride is that of Dumas (*Ann. Chim. Phys.*, 1826, xxxi., p. 466; xxxiii., 376), who allowed chlorine to pass in a tube over a heated mixture of powdered melted boric acid and charcoal.

It seemed to be of interest to ascertain how the boron prepared by the above method would behave towards chlorine. The apparatus which was used was the following:—A hard glass tube, as used for combustions, about 4 to 8 inches longer than the combustion-furnace to be used, is drawn out at one end and bent almost at right angles. This part is attached to a Peligot's tube, which is surrounded by a freezing mixture of ice and salt. All the necessary joints are made by means of smooth and closely-fitted corks. The air-dry boron is loosely spread in a combustion-tube, so that it is one-fourth inch in thickness all through; and as the boron must be thoroughly dry the water is driven out by heating in a stream of hydrogen, also allowing it to cool in the same. Carbonic acid cannot be used, as boron reduces it completely to carbon monoxide, as noticed by Lorenz (*Ann. Chem.*, 1889, ccxlvii., p. 226). After the tube has cooled the hydrogen is forced out by a stream of dry air, and the larger end of the tube then connected with a chlorine generator. The chlorine is prepared from manganese dioxide and hydrochloric acid, and best regulated so that a slow but steady stream is obtained. The whole apparatus is filled with washed and dried chlorine gas before heat is applied, sufficient for producing a slight glow in the tube. A liquid having the colour of chlorine gas condenses in the Peligot's tube, which is best connected with a good drawing chimney, as some of the trichloride goes through uncondensed. The colour of the liquid is due to dissolved chlorine, which is removed by shaking the liquid with mercury in a sealed tube, which can also be used for distilling. After the liquid has become perfectly colourless, which takes about two days, the tube is opened, and, by means of a closely-fitting cork, a narrow glass tube, twice bent at right angles, is attached. The one arm of the tube which is used as a condenser is to be about 20 inches long, and projects to the bottom of the receiving vessel, which is surrounded by a freezing mixture of ice and salt. The best receiver is a wide glass tube about 25 inches long and about 5 inches below the orifice drawn out, so that the condensing tube just moves freely in the opening. The distillation is best carried on by means of warm water, very slowly, so as not to lose too much of the chloride—this boiling at 18° C.

The yield of the chloride by this process is as follows:—By using 8 grms. of magnesium powder for reduction the boron gave 15 grms. of the chloride, the theoretical yield being 26 grms.

NOTICES OF BOOKS.

A Handbook of Modern Explosives: being a Practical Treatise on the Manufacture and Application of Dynamite, Gun-cotton, Nitroglycerin, and other Explosive Compounds, Including the Manufacture of Collodion-Cotton. By M. Eissler, Mining Engineer and Metallurgical Chemist. London: Crosby Lockwood and Son.

The author of this work published about five years ago, in New York, a treatise on "The Modern High Explosives."

The book now before us, though very similar in its general character, is drawn up with more reference to the demands of a British public, containing, as it does, an abstract of the Explosives Act now in force in this country, the instructions, issued under the authority of the Home Office, for determining the stability of explosives, and the forms of application for authority to manufacture or import any new explosive. The work also contains the processes of Captain Hess for the analysis of explosives. Here we notice, as far as gun-cotton is concerned, some decided improvements as compared with earlier practice. Thus, in determining the mineral matter, the sample is first impregnated with paraffin, upon which it burns away quietly, without any projection or loss of the ash.

The separation of trinitrocellulose from cotton fibres which have escaped nitration is effected by taking a portion of the gun-cotton, after the mono- and dinitrocellulose have been dissolved out in the usual manner with absolute alcohol and ether, and repeatedly boiling in an excess of a saturated solution of sodium sulphate; any raw cotton existing in the sample remains undissolved in company with the insoluble mineral matter.

The author, however, points out, on the authority of Böckman, that neither gun-cotton, collodion-cotton, nor nitro-glycerin can be viewed as true nitro-compound, as, for instance, is picric acid. They are rather to be regarded as ethers of nitric acid.

Concerning melinite, we find some more definite information than has yet been discovered. It has generally been described as a mixture (or compound) of which picric acid is merely one of the ingredients. Here, however, melinite is said to consist simply of picric acid compressed and then either agglomerated with an aqueous solution of gum arabic or a fatty body, or cast by fusion at 130° to 145° and poured into the moulds. The discovery is announced that picric acid alone, such as it is found in commerce, "is one of the most powerful explosives that can be conceived; its explosive force is greater than that of compressed gun-cotton and the different forms of dynamite, whilst its insensibility to shock, as well as its stability, are very remarkable."

He demonstrates that "the maximum force of this kind, contrary to what has been believed, does not coincide with the chemical formulæ which corresponds to complete combustion, but, on the contrary, with the combustion which yields carbonic oxide."

The advantages claimed for picric acid, especially for military uses, are:—Absolute chemical stability, *i.e.*, non-susceptibility to spontaneous decomposition or elementary change; absolute physical stability, *i.e.*, non-liability to congelation, exudation, liquefaction, or evaporation; it is non-hygroscopic, insensible to the most extreme variations of natural temperature; free from danger in manufacture, manipulation, and transport; and insensible

(in shells) to the shock of the discharge of cannon. We are told that a substance called "Lydite," much resembling melinite, is under examination by our Government.

The subject matter of this work has its painful sides. The author speaks of the "great benefits which have been conferred upon the world at large by the invention of these explosives," and he expresses the hope that they may find their "exclusive employment" in the operations of the civil and mining engineer.

We cannot, however, help expressing the fear that such inventions have occasioned, and may yet occasion, more harm than good. Without dynamite the "dynamitard" could not have existed. Since, however, these compounds have come into existence, no nation can afford to ignore them, and hence Mr. Eissler's work is of unquestionable value.

Electrical Distribution of Heat, Light, and Power. By Harold P. Brown, Electrical Engineer. With a partial List of Deaths from Electrical Lighting Apparatus, with an Address by John Murray Mitchell, Counsellor-at-Law, on Legislative Control of Dangerous Electrical Currents. New York: J. W. Pratt and Son.

This pamphlet consists essentially of an address delivered by the author on June 4th last, before the International Medico-Legal Congress. Its object is essentially a protest against the use of alternating currents, especially if at high tensions, and, as far as we can judge, most of all against the Westinghouse system. He contends that burying the wires is no protection. Yet, we must say, after carefully reading over the list of fatalities, some of them never could have happened if the wires had been laid underground. These men were killed "by touching telegraph wire *hanging* over Westinghouse circuit," by "trailing alternating current wire," by "touching dangling telegraph wire," "touching hanging telegraph wire," "touching dangling telegraph wire." We submit that there ought not to be any trailing, hanging, or dangling wires.

Upon experts, or "professional scientists," Mr. Brown is very severe. He writes that a representative of this class believes that "his opinion must necessarily coincide with the wishes of the corporation which retains him, no matter if scientific accuracy must be sacrificed." Again, he tells us that "when the water-gas question was under discussion some years ago, one of this fraternity gave his written opinion to a New York gas syndicate that a small percentage of carbonic oxide in illuminating gas was necessarily fatal. Shortly after, he was 'acquired' by a water-gas system, and testified without hesitation that 32 per cent of carbonic oxide need not be regarded as detrimental." If such misrepresentation of science exists, in New York or elsewhere, the fact is greatly to be deplored and protested against.

May we, without touching too strongly national susceptibilities, remark that recklessness in matters concerning the public safety is more strongly manifested in America than in Britain? Precautions, if costly, are more generally neglected, and such neglect on the part of a wealthy and influential company is either condoned or there is a difficulty in bringing the offenders to justice.

It by no means follows that if high tension alternating currents are introduced among us that they will occasion such accidents as Mr. Harold Brown enumerates.

On the Ventilation of Schools: a Lecture delivered before the College of State Medicine, May 22nd, 1889. By Sir Henry E. Roscoe, M.P., F.R.S., D.C.L., LL.D. London: T. W. Danks and Co.

The publication of this lecture may be called very timely, in view of the recent disclosures concerning the sanitary, or rather unsanitary, condition of not a few primary schools. A glance at its date, however, will show that it was not written with any reference to the late revelations. On the contrary, the author seems to be of opinion that Board Schools, in the matter of ventilation at least, are in a better condition than those establishments to which he applies the offensive name of "private *adventure* schools," a term invented by school board authorities. His enquiries do not, it seems, extend to boarding schools, where, we suspect, the results, if procurable, would not be reassuring.

Among the important points brought to light is the fallacy of the routine assumption that the atmosphere of the upper part of a dwelling room, above the level of the chimney-piece, was richer in carbonic acid than the lower part. This view was plausible, but it does not stand the test of actual analysis.

The table of the volumes of carbonic acid contained in 10,000 vols. of air in different localities will be likewise a revelation to many readers; whilst the normal proportion is given as four. That of the Madrid hospitals ranges from 27 to 43; that of the London theatres 8·2 to 32; and that of mines to 78·5. It will also be a surprise that the average for London, 4·4, exceeds that of Manchester, 4, whilst in the Metropolitan tunnels the proportion is 14·5.

Sir H. Roscoe shows likewise the fallacy of the supposition that the amount of carbonic acid in any given locality varies as the organic matter. This is proved, *inter alia*, by the fact here mentioned, that "during a course of crowded popular lectures in the new lecture theatre of University College, Dundee, an average of only four microbia per litre was found, as compared with an average of about 3 when the room had remained empty. Nor did the average rise beyond 6 per litre when the room was left unventilated during the lecture, whilst the carbonic acid rose to nearly 40 vols. per 10,000.

It is shown that a mere determination of readily oxidisable matter in a given volume of air is not sufficient, since the various methods proposed for this purpose fail to distinguish septic or pathogenic matter from that which is relatively harmless. Hence, in all comparative examinations of the air of different localities the bacteriological methods of Pasteur, Koch, and Klein have to be brought into play. Here we come upon the startling fact that in a "naturally ventilated" school at Dundee the number of bacteria in 18 litres of air reached 1510, whilst in the bed-rooms of the one-room houses of the same town, the proportion was only 585, a number, of course, far too high, but small in comparison with that in the schools.

The origin of the microbia in the air of houses and schools is still undecided. They are not given off to any appreciable extent in the ordinary respiration of healthy persons. Neither does the floor, with the loose dirt lying about on it, appear to be at fault. Scrubbing the floor does not appear to have any permanent effect in diminishing the microbia. Thus, two similar school-rooms were taken: one was scrubbed once a week for five weeks, and the other was left unscrubbed. The total effect of the scrubbing was nil. Other things being equal, there are fewer bacteria in the air on damp or still days than on dry or windy days.

The author is of opinion that enlarged air-room per head and improved ventilation in primary schools would "pay" our educational authorities. Into this question the Chemical News cannot enter, though we may remark that the money which has been expended on board schools, if it had been honestly and judiciously laid out, would have been amply sufficient for the improvements which Sir H. Roscoe and Dr. Carnelley recommend.

Seventh Annual Report of the Board of Control of the New York Agricultural Experimental Station for the Year 1888. Albany: Troy Press Company.

From the Report of the Executive Committee it would seem that the Station, prior to its purchase by the State, had been allowed to fall into a state of ruin and neglect.

According to the Treasurer's Report the Laboratory cannot be accused of extravagance, its outgoings for the past twelve months not exceeding the modest sum of 25¾ dollars.

A startling piece of information is that eggs are imported *into* the United States on a vast scale, the total for 1885—the last year given—being 16 million dozens. Whence they came we do not learn.

Trials have been made at the station with various compounds as insectides. The chemicals used were "Paris green," a copper arsenite, "London purple," a residue from the manufacture of magenta by the Medlock process, and the "Zoëktein" poison. The substance bearing this alarming name is an arsenical compound of unknown composition.

For the "codling-moth" (*Carpocapsa pomonella*), Paris green proved the best remedy.

The "cabbage maggot" was attacked with salt water, with McDougall's sheep dip, diluted with 5 parts of water, with Zoëktein, and with kerosene. The brine had no effect; the sheep-dip did not harm the insects, but was fatal to the plants, whilst Zoëktein and kerosene destroyed both.

Sodium thiosulphite and potassium sulphide proved useful against parasitic fungi. Calcium sulphide, on the contrary, was found of doubtful value.

The trials with manurial matters led to the adoption of 17½ cents per lb. as the value of ammoniacal nitrogen; 16 as that of nitric nitrogen. Organic nitrogen ranges from 16½ in dried ground fish, blood, and cotton seed, to 8 in horn-shavings and hair. Phosphoric acid, soluble in water or in ammonium citrate, is valued at 8 cents per lb., but that in finely ground mineral phosphate only at 2. Basic slag does not seem to have been tried.

The sale of manures in many of the States is subject either to a license, which may reach 500 dollars, or in others to a fee for analysis by the State agricultural chemist.

Manual of Assaying Gold, Silver, Copper, and Lead Ores With One Coloured Plates and Ninety-four Illustrations on Wood. By Walter Lee Brown, B.Sc. Third Edition. Chicago: E. H. Sargent and Co.

The author takes exception to existing treatises on assaying, either as antiquated in their methods and apparatus, or as being more books of reference than manuals.

Mr. Brown begins with a description of the apparatus used in assaying. It might, perhaps, be said that figures of balances and weights are scarcely necessary in these days. The explanation of the "assay-ton" is very clear and is given both to suit the metric system, the American ton (2000), and the British ton of 2240 lbs.

He describes a furnace which he has constructed and named the "Monitor," but which he recognises as an application of a principle due to Mr. Fletcher, of Warrington. As for crucibles and muffles, he recommends those of the Morgan Crucible Co., Battersea.

Among the apparatus mentioned is a "casserole," which is a deep porcelain capsule or crucible fitted with a handle.

In the list of reagents and the remarks as to the examination of their purity we find nothing calling for remark.

In the section of the book which treats of the practical operations of assaying, the author remarks that the colours shown by the interiors of scorifiers are often characteristic of the ores operated upon, and, in conjunction with the colours of the cupels after cupellation, make valuable tests. Of these he describes and figures very beautifully the colours given by ores containing uranium, chrome, manganese, copper, iron, and lead. Under lead he remarks that vanadium, cadmium, and bismuth give the same shades. The colours given by nickel and tellurium he does not consider very characteristic.

The instructions for the assay of gold and silver ores are fully on a level with the practice of the day, every operation being fully and clearly described.

Concerning the assays of copper and lead by the dry way, he admits their inaccuracy, and recognises that, especially as far as copper is concerned, they are being everywhere superseded by the more exact volumetric and electrolytic methods, which, accordingly, he describes in the appendix.

We must, however, take exception to the following passage:—"In a certain sense no one cares to know the ultimate amount of metal that an ore contains. What is desired in practice is the *yield* under the most skilful treatment, and this information is approximately obtained by fire for copper."

Now an intelligent metallurgist wishes to know the exact amount of metal in his ores that he may see how near his working processes come to perfection. The dry assay—Cornish at least—shows *less* copper than can be obtained on the large scale, in a proportion which is the greater the poorer the ore, and, according to the vicious system of the English copper trade, this excess over and above the results of the assay is the smelter's profit.

The appendix also contains lists of the principal gold and silver minerals found in the United States, as also of those which may prove auriferous or argentiferous. We venture to suggest that a similar catalogue for Australasia and South Africa would prove very valuable if carefully compiled. We cannot do other than recommend this book as valuable and trustworthy.

Introductory Lessons on Quantitative Analysis, suitable for the Examinations of the Science and Art Department and the University of London. By John Mills and Barker North.

The work before us is purely an outcome of our vicious system of secondary education. There is nothing in it, however accurate, which cannot be found again and again in other accessible works. We are therefore compelled to ask, as in case of the majority of chemical manuals issued, *cui bono?* The authors are, in their teachings, avowedly examinational. They write for "students in evening classes who have but little time to spare in acquiring such knowledge." Now, to assist people in "passing" who have not time to "know" is an aim which we cannot applaud, and the existence of such a class of persons is of little credit or advantage to Science, to the nation, or to themselves.

The Micro-Organisms of Fermentation practically considered. By Alfred Jörgensen. Edited from the German by G. Harris Morris, Ph.D., F.C.S., F.I.C. With an Introduction by Horace T. Brown, F.C.S., F.I.C. London: F. W. Lyon.

The Carlsberg Laboratory, founded and endowed by the late eminent Danish brewer, J. C. Jacobsen, has become the seat of most important researches in the chemistry—or we had better say the chemico-biology—of fermentation. From it have emanated the studies of Dr. E. C. Hansen, which have marked a turning-point in the industry of brewing, and subsequently of Dr. Jörgensen, the author of the work before us.

In the Introduction an objection is very justly raised against the term bacteriology as applied to a study of the action of microbia upon organic matter. Those organisms with which the brewer and the manufacturers of wine and vinegar are chiefly concerned are not bacteria. At the same time the study of these ferments, as taken up by Pasteur, has been the starting point of this branch of biology. It is also pointed out in this Introduction as a result established by the labours of Hansen that the "supposed morphological differences which have been relied on to establish the various species and varieties of

the *Saccharomycetes* are in the highest degree illusory and untrustworthy; in fact, that species having very different physiological functions may assume forms which it is impossible to distinguish by a mere microscopical examination."

We have had recent proof of the importance of this variation in function, since it has been found that the different aroma of wines depends less on the species of grape, or soil, or climate than on the variety *Saccharomyces ellipsoideus*, otherwise known as *Mycoderma vini*.

Bacteria, as distinguished from the *Saccharomyces*, have an injurious effect alike in the production of wine, beer, and vinegar. The author lays great emphasis on the preparation of pure ferments, the methods for which are mainly due to Hansen. Those methods and the consequent improvements are not, as the author shows, restricted to bottom-yeast, but can be extended also to top-yeast, as used in English breweries. The instructions for the performance of experiments with the micro-organisms are admirably clear and full. The author calls attention to unfortunate mistakes which have been committed, and shows how the like may in future be avoided. Concerning disinfectants and sterilisers he reminds the reader that even mercuric chloride in dilute solutions is not so certainly and rapidly effective as it has been supposed. A solution of 1 in 300 is needed to stop the growth of some *Schisomycetes*.

Appended to the work is a copious bibliography of the subject.

English brewers ought to feel themselves much indebted to Dr. G. H. Morris for placing Jörgensen's work within their reach.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

SIR,—It may be interesting to Mr. Thompson to know that the deviations of which he gives an account in the CHEM. NEWS (vol. lx., p. 295), are many thousand times as great as any that can be due to gravitation alone. While they may be interesting, as showing to what a great extent magnetism, electrification, convection currents, or tilting may give rise to spurious deflections, they cannot have any bearing on the question of gravitation or its cause.—I am, &c.,

C. V. BOYS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 24, December 9, 1889.

The Nitrification of Ammonia.—Th. Schlœsing.—The author concludes that the nitrites are not merely products of an obstructed and incomplete nitrification, but they are in themselves an obstacle to the normal function of the nitrifying organisms. When nitrites are present there is a distinct escape of gaseous nitrogen. It does not, however, follow that the nitrites are the cause of the escape of nitrogen. It may be that the escape of the nitrogen and the presence of nitrites are merely simultaneous, and both due to one and the same cause. The destruction of nitrites in reducing media furnishes, according to the nature of such media, nitrous acid, nitrous and nitric oxide, free nitrogen, and even ammonia. Reciprocally he conceives that an incomplete oxidation of ammonia or of organic nitrogen yields merely free nitrogen or nitrous acid, or both simultaneously.

Combinations of Potassium and Sodium with Gaseous Ammonia.—A. Joannis.—It has been previously proved by Gore that potassium and sodium are capable of dissolving in liquefied ammoniacal gas. This liquid, as the gas escapes, deposits a solid body of a deeper red than copper. In this manner the author obtains solid sodammonium or potassammonium. The author is engaged with the further study of these bodies.

Ammoniacal Mercury Cyanides.—R. Varet.—The action of ammonia upon mercuric cyanide yields the two compounds $Hg_2Cy_2,2NH_3$ and $Hg_2Cy_2NH_3$. On operating in an aqueous solution and crystallising below 0° we obtain their hydrates.

Simultaneous Determination of Sulphur and Carbon in Organic Substances containing Sulphur.—L. Prunier.—This paper will be inserted in full.

An Isomer of Carballylic Acid.—E. Guinochet.—The acid obtained is certainly an isomer of the carballylic acid hitherto known, as is found by its composition, its physical properties, its capacity of saturation by bases, and its calcium and barium salts.

Two New Sugars obtained from Quebracho.—C. Tanret.—One of these, obtained directly, has been named quebrachite, and has the composition $C_{14}H_{14}O_{12}$. It does not ferment with beer-yeast. It is lævo-rotatory, and does not react on Fehling's solution. On splitting up it yields a lævo-rotatory inosite.

Researches on Carotine, and its Probable Physiological Function in Leaves.—M. Arnaud.—The author has determined the proportion of carotine in a considerable number of plants, and suggests that, like the hæmoglobine of blood, its function depends on its avidity for oxygen.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 9.

Action of Water on Stannic Chloride.—Leo Vignon.—When stannic chloride and water are mixed we obtain a solution of stannic oxide in dilute hydrochloric acid. This stannic oxide, which is very unstable, tends to become polymerised. In time the polymerisation reaches a certain state of equilibrium, which is a function of the dilution, the temperature, and the chemical composition of the liquid.

Methods of Analysis of the Feed-Waters of Steam-Boilers, with a View to the Use of Anti-Incrustation Agents.—Leo Vignon.—The author, approving of the proposal to use sodium carbonate as a de-incrustation agent, recommends a method for ascertaining the quantity needed. His reagents are saturated lime-water, which should be pure, and which contains, per litre, 1·80 grms. of $Ca(OH)_2$; a concentrated alcoholic solution of phenolphthalein, obtained by dissolving 5 grms. of neutral phenolphthalein in 100 c.c. of alcohol at 93°. A solution of calcium chloride, thoroughly neutral, containing about 5 grms. per cent. A solution of sodium carbonate containing 1 grm. sodium carbonate in 1 litre distilled water. For determining the carbonic acid he places in a stoppered test-jar 50 c.c. of distilled water and 10 drops of the alcoholic solution of phenolphthalein. In another test-jar he places 50 c.c. of the water in question, 10 drops of the solution of phenolphthalein, and 5 c.c. of the solution of calcium chloride. The first jar is then coloured by means of 0·2 to 0·5 c.c. of lime-water measured in with a burette. The colouration produced by the lime-water will disappear very rapidly at first, on agitation, so long as the carbonic acid in the liquid is in sufficient excess. Towards the end of the reaction the combination of the lime with the

carbonic acid is slower, whence the liquid must be frequently added, and the lime-water is added at longer intervals. When the colouration of the water under examination reaches and retains that of the standard—which may require an hour—the standard is made up with distilled water to the same volume as the water under examination, and lime-water is added to the less highly-coloured liquids, so as to equalise the tints; the two test-jars are then compared colorimetrically, and if examined against a white background, differences due to the presence of 0·1 c.c lime-water are easily detected. When the colourations are identical the two liquids contain the same quantity of free lime. The difference between the lime consumed by the standard liquid and the water under examination represents the quantity of lime absorbed by the free carbonic acid or that half-combined. To find the quantity of sodium carbonate which must be added to a boiler to prevent incineration, it is necessary to know the quantity of free or half-combined carbonic acid contained in 1 litre of the feed-water, and the quantity of sodium carbonate requisite to convert the calcium chloride and sulphate into insoluble carbonates.

Formation of Chloro-benzenes by the Superchloridation of Anisol.—L. Hugounenq.—This paper does not admit of useful abstraction.

Journal fur Praktische Chemie.
New Series, Vol. xl., 1889, Nos. 14 and 15.

The Action of Tin Salt upon Diazo-hydrocarbonates and Some Reactions of Diazoimido-hydrocarbons.—C. Culman and K. Gasiorowski.—This memoir does not admit of useful abstraction.

New Apparatus for Electro-chemical Investigations.—N. von Klobukow.—The author describes and figures stirring-arrangements in electro-chemical apparatus.

Calorimetric Researches by F. Stohmann.—Researches on the thermic value of carbon-acids of the aromatic series.

On Oriental Enamels on Tiles and on their Imitation.—J. Boeck.—The author compares the permanence of the enamels to be found in the Royal Mosque of Ispahan, built by Abbas the Great at the beginning of the 17th century, and those of the Alhambra, dating from the beginning of the 13th century, with the brief duration of external enamel work in Northern Europe, and admits that climate is, to a great extent, the cause of the difference. He gives the composition of a turquoise-blue enamel from the Mosque Schach Zende, built by Timur, as—

SiO_2	53·53
CuO	3·51
PbO	17·90
CaO	3·00
MgO	0·33
SnO_2	6·86
K_2O	3·51
Na_2O	7·27
Fe_2O_3 / Al_2O_3	3·11
	99·02

and traces of As and Mn. He considers that there are only two possibilities of producing weather-proof enamelled tiles; either the clay must be burnt very compact, or its pores must be filled up in some manner so as to exclude the action of moisture and frost.

On the Regularities in the Apposition of Haloid Compounds on Non-saturated Acids.—A. Michael.—The author concludes that in organic compounds of the fatty series which contain several hydroxyls, that hydroxyl is first replaced by halogens, which is united with the relatively most positive carbon, or as it may be otherwise expressed, the hydroxyl of the most basic carbinol. In organic compounds which contain several symmetrically arranged atoms of the same halogen, that halogen is first replaced by another atom or a group, which is united with the most negative carbon. In the apposition of halogens and hydrocyanogens to the oxides of polyvalent organic radicles, the halogen and the cyanogen pass to the most positive carbon. If a reagent adds itself to an unsaturated and non-halogenous compound of the fatty series, its negative part goes to that unsaturated carbon which is relatively the most positive. In the addition of hydrohalogens to non-saturated acids of the fatty series, the halogen combines exclusively with the unsaturated carbon which is relatively the most positive.

MISCELLANEOUS.

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Thursday, Jan. 2nd.—Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
Friday, 3rd.—Geologists' Association, 8.
Saturday, 4th.—Royal Institution, 3. "Electricity," by Professor A. W. Rücker, F.R.S.

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INDEX.

ABERDEEN University, 148
Aberystwyth, University College, 139
Acenaphthene, oxidation products of, 59
Acetylation of cellulose, 254
Acetylcarbinol, 280
Acetyl derivatives of cellulose, 163
Acid, bromonaphthalene-sulphonic, 57
carballylic, isomer of, 317
carbonic, detection of, 37
diethylamidopropionic, 72
gas, carbonic, solubility of, 49
hydrochloric, action of, 121
and chlorine, methods of producing, 221
and water, simultaneous synthesis of, 246
hydrofluoric, purification of, 252
nitric, conditions of action of, 13
magnetic rotation of, 253
nitrous, solidification of, 49
oxamic, and oxamide, new process for preparing, 245
phenol-disulphonic, 185
phosphododekamolybdic, 169, 177, 188, 201, 215
phosphoric, determination of, 12, 74
volumetric determination, 310
pyrogallic, new reagent for, 282
sulphuric, determination of, 19
improvement in the manufacture, 282
tetrahydrate of sulphuric, isolation of, 253
Acids, camphoric, chemistry of, 307
dioxyphosphinic, 49
fatty, and soaps, action of in the animal body, 197
in oils, free fatty, 34
phenolsulphuric, 97
phosphotungstic, 161
sulpho-conjugated, 62
Agricultural College, Cirencester, 142
"Agricultural Experimental Station, Report" (review), 315
Air, ground, 258
Albumen, cause of error in detecting, 130
Alcohol, determination, 109
in ethereal oils, 103
Alcoholic fermentation of honey, 197
Aldehyds, action of, 302
"Alkali Works Regulation Act" (review), 60
Alkaline nitrites, preparation of, 2
Alkaloid a novel, 73, 114
Allen, A. H., "Commercial Organic Analysis" (review), 36
Alloys, nickel and tungsten, magnetism of 312
of iron and silicon, 273
Almonds, bitter, natural oil of, 109
Althausse, M., and G. Krüss, composition and the absorption-spectrum of organic compounds, 240
Alum in bread, 133
test for, 134
Alumina and ferric oxide, determination of, 98
phosphorescence of, 65
Aluminium alloys, manufacture of, 211, 225, 241
manufacture from cryolite, 199
reduction of, 292
Ambühl, G., examination of butter, 109
"Amines" sewage process, 157, 184, 196, 207, 221, 233, 245, 257
Ammonia, nitrification, 184, 317
"Ammonia and Ammonium Compounds" (review), 304
Ammoniacal copper sulphate, action of, 246
Ammonio-cobaltic tungstates and vanadates, 81
Ammonium sulphide precipitate. qualitative analysis of, 272
Amyl iodide, purification of, 12
Amylaceous bodies, combinations of copper oxide with, 209
Analysis, organic, modification of, 74
rapid, of Prussian greens, 73
of cocoa, 234
of concentrated superphosphate, 91
of crude materials containing tartaric acid, 109
of feed-waters of steam-boilers, 317
of glasses, 14, 33, 41
of iron and steel, international standards for, 247
of lead peroxide, 97
of milk, 213, 233, 245, 257
of some cistern deposits, 56
of sugars, 306
of the raw materials and the products of siderurgy, 270
of water, 203, 249, 281
"Analysis, Commercial Organic" (review), 36
"Analysis, Qualitative" (review), 245
"Analysis, Quantitative" (review), 316
"Analytical Tables, Coloured" (review), 244
Anhydrous platinum bifluoride, 291
Animal heat, 282, 293
Aniline, mono-methyl, 11
reactions of dimethyl, 121
"Aniline Black, History of" (review), 72
Antifebrine, detection, 109
Armstrong, H. E., hydration of cyanides, 59
molecular weight of substances in solution, 46
and W. P. Wynne, isomeric change in the naphthalene series, 58
Arnaud, M., carotine, 317
crystalline digitaline, 258
tanghinine, 24
Arnold, R., and H. G. Coleman, "Ammonia and Ammonium Compounds" (review), 304
Aromatic nucleus, new sugar with, 293
Arsenic and copper, determination of, 133
Arsenical water of Court St. Etienne, 67
Artesian waters of the French Sahara, origin, 209
Ashe, I., dimidium, 235
Association, British, 120, 123, 151, 161
"Assaying, Manual" (review), 316
Atomic considerations, 299
weight of copper, 110
zirconium and its, 6, 17, 32
weights, classification of, 164, 178
of simple bodies, 208
Attfield, J., "Chemistry," (review), 11

BAILEY, G. H., zirconium and its atomic weight, 6, 17, 32
Balance, improved, 12
Bangor, University College, 140
Barium cobaltites, 49
malonates, 37
sulphate from mine-water, 80
Basic salts, constitutions, 283
Batteries, storage, 100
Baumert, M., detection of chicory in coffee, 197
Bedson, P. P., manufacture of aluminium from cryolite, 199
Bell, Sir I. L., address to chemical section, British Association, 151
Benedikt, R., and E. Knecht "Chemistry of the Coal-Tar Colours" (review), 161
Benker, F., improvement in the manufacture of sulphuric acid, 282
Benzol, constitution of, 210
Benzoquinone, reaction, 187
Bernthsen, A., "Text-Book of Organic Chemistry" (review), 281
Berthelot, D., employment of electric conductivity for the study of acids of complex functions, 288
fixation of nitrogen, 161, 184
influence of electricity on vegetable mould, 161
raffinose, 221
reciprocal displacements between oxygen and the halogens, 251
and M. Moissan, combination-heat of fluorine and hydrogen, 97
and P. Petit, animal heat, &c., 282
formation-heats of the nitrites, 24
thermic researches on isomeric nitrocamphors, 62
Besson, A., certain reactions of nitric oxide, 121
existence of phosphonium sulphate, 246
Bevan, E. J., and C. F. Cross, acetyl derivatives of cellulose, 163
acetylation of cellulose, 254
conditions of action of nitric acid, 13
constituents of flax, 280
Bidwell, S., electrification of a steam-jet, 303
Bielkin, M., active principles of Panama bark, 120
Birhans, F., solidification of of nitrous acid, 49
Birkbeck Literary and Scientific Institution, 147
Bismuth, electrical resistance, 10
Blood, traces of, spectroscopic demonstration of, 50
Blum, L., determination of carbon in the irons of commerce, 167
precipitation of magnesia, 239
separation of small quantities of manganese from a large quantity of lime, 162

Boeck, J, oriental enamels on tiles and their imitation, 318
Borax, action of, 157
Borneol and camphor, separation of, 25
specific volume of, 114
Börnstein, E., "Industry of Colours" (review), 159
Boron, 313
Bottomley, J. T., expansion of wires, 10
and A. Tanakadate, thermo-electric position of platinoid, 77
Boys, C. V., Cavendish experiment, 99, 111
pendulum experiments, 317
Braithwaite, J., "Retrospect of Medicine" (review), 61
Bradford Technical College, 141
Bréal, E., fixation of nitrogen, 257
Bristol, University College, 141
British Association, 120, 123, 151, 161
Bromide, ferric, reduction, 270
Bromides, pentamethylene and tetramethylene, 133
Bromine, volumetric estimation, 259
Bromo-naphthalene sulphonic acid, 57
Bronze, magnesium, 272
Brown, H. P., "Electrical Distribution of Heat, Light, and Power" (review), 315
W. L., "Manual of Assaying" (review), 316
Brownian movement, 62
Brucine and strychnine, separation of, 185
Brullé, R., reactions of the oils with silver nitrate, 62
Brun, E., copper oxybromide, 49
Brunner, H., sodium nitroprusside, 168
Bruylants, M., alum in bread, 133
fraudulent panification, 120
Bullock, C., preparation and properties of metallic manganese, 20
Burton, C. V., physical bases for the theory of errors, 2, 30
Butter, 109
Butterflies, yellow pigment in, 57
Butyryl chloride, action of, 45

CADMIUM from zinc, electrolytic separation of, 9
sulphide, 62
Cailletet, L., and E. Colardeau, condition of matter near its critical point, 24
Calorimetric investigations, 121
researches, 210
Cambridge University, 136
Camphor and borneol, separation of, 25
specific volume of, 114
monochlorised, 97
new monobromated, 185
Camphoric acids, chemistry of, 307
Cane-sugar, &c., new reagent for, 282
"Capillary Analysis" (review), 159
"Capillary Analysis, Appendices to the Investigation on" (review), 158
Carballylic acid, isomer of, 317
Carbolic disinfectants, 68
Carbon compounds, coloured reactions of, 104
in iron, determination of, 167
monoxide, new reaction for, 110
Carbonic acid, detection of, 37
gas, solubility of, 49
Carles, P., variable causticity of phenol, 120
Carnegie, D. J., nature of the reaction between solutions of ferric chloride and potassium iodide, 87
new crystalline hydrate of thallic oxide, 113
titration of ferric salts, 159
Carnot, A., ammonio-cobaltic tungstates and vanadates, 81
separation of cobalt and nickel, 54
volumetric determination of silver, 90
Carotine, 317
Casein, fission products of, 62
Cavedoni, L., examination of vermicelli for foreign colours, 85
Cavendish experiment, 99, 111
Cazeneuve, P., camphor, monochlorised, 97
new monobromated camphor, 185
oxidising action of nitroso-camphor, 85
use of potassium permanganate, 121
Cellulose, acetyl derivatives of, 163
colloid, 24
Cement, 162
Portland, practical study on, 270
Chabrié, C., synthesis of certain oxygenated selenium compounds, 221
of some selenium compounds, 84
Chapman, A. C., zinc dextrosate, 57
analyses of some cistern deposits, 56
Charterhouse Science and Art Schools, 147
Chemical composition of the rock-salt of Roumania, 121
laboratory of Wiesbaden, 134
lectures, classes, and laboratory instruction, 147
literature, report of committee on indexing, 224
section of British Association, address, 151
Society, 45, 56, 253, 264, 278, 301
"Chemical Science, Introduction to" (review), 292
"Chemical Technology" (review), 219
Chemistry, attempt to apply one of Newton's principles, 1, 15, 30
Institute of, 109
Liverpool College of, 143
present method of teaching, 170, 181, 193, 204, 226, 224, 296
schools, 135, 160
Service, 160
technical training in, 63
under high pressure, 42
"Chemistry" (review), 11
"Chemistry of the Coal-Tar Colours" (review), 61
"Chemistry, Organic, Text-Book of" (review), 281
"Chemistry, Service" (review), 220
"Chemistry, Watts' Dictionary of" (review), 256
"Chemistry, Watts' Manual, (review), 220
Chemist, libel on a, 62
Chenevier, A., rapid analysis of Prussian greens, 73
Chicory in coffee, detection of, 197
Chloride, butyryl, action of, 45
stannic, action of water on, 317
of mercury, toxicologica search for, 133
of zinc, 122
Chlorine and hydrochloric acid, method of producing, 221
water, rate of decomposition by light, 271
Chloroform, solubility of carbonic acid gas in, 49
Chrome, new process for mordanting, 209
"Chromelectro-Chemical Communications" (review), 159
Chromites of zinc and cadmium, 72
Chromium chloride, convenient preparation of, 85
Cinnamic acid series, alloisomerism in, 210
Cirencester, Royal Agricultural College, 142
Cistern deposits, analysis of some, 56
City and Guilds of London Institute, 147
School of Science and Pharmacy, 147
Clarke's soap test, 132
Claus, A., constitution of benzol, 210
Clayden, A. W., photographs of lightning and black electric sparks, 10
Clayton, E. G., vermilion or vermillion, 160
"Clinical Chemistry of Urine, Outlines of" (review), 220
"Clinical Use of Prisms" (review), 292
Clowes, F., deposits of barium sulphate from mine water, 80
Coal, formation of, 263, 275
"Coal-Tar Colours, Chemistry of" (review), 61
Cobalt and nickel, nature of, 8
separation of, 54
passivity of, 157
Cobaltites, barium, 49
Cocaine from animal remains, separation of, 110
Coffee, detection of chicory in, 197
Cohen, J. B., and T. Ewan, oxidation products of acenaphthene, 59
Colardeau, E., and L. Cailletet, condition of matter near its critical point, 24
Colleges and Universities, 135
Colman, H. G., and R. Arnold, "Ammonia and Ammonium Compounds" (review), 304
Colorimetric method for the determination of nitrates, 261
Colour-blindness, experiments in, 247
Colours produced during the tempering of steel, 190
"Colours, Industry of" (review), 159
Colson, A., application of thermochemistry, 282
Copper and arsenic, determination of, 133
atomic weight of, 110
oxide with amylaceous bodies, combinations of, 209
oxybromide, 49
sulphate, ammoniacal, action of, 246
electrolysis of, 24
Copra and palm oils, assay of, 258
Cornish uranium mine, 234
Coste, J. H., and R. Meldola, monobenzyl derivatives of the phenylenediamines, 57
Cotton dyed with lead chromate, poisoning by, 74
Cow's milk, utilisation of, 197
Crafts, J. M., and C. Friedel, decomposition of the sulpho-conjugated acids, 62
Craig, G., estimation of silica, 227
Crampton, C. A., pipette for measuring juices for polarisation, 55
Cripps, R. A., iodine absorption of essential oils, 236, 281
Crookes, W., recent researches on the rare earths, 27, 39, 51, 63
W. Odling, and C. M. Tidy, London water supply, 34, 104, 166, 416, 252, 309
Cross, C. F., and E. J. Bevan, acetyl derivatives of cellulose, 163
acetylation of cellulose, 254
conditions of action of nitric acid, 13
constituents of flax, 280
Cryolite, manufacture of aluminium from, 199
Crystals, improved method for the formation of regular, 237
Crystalline cobaltous and ferrous hydrates, 133
Cyanides, hydration of, 59
Cyano-camphor, researches on, 62

DAGGER, J. H. J., manufacture of the alloys of aluminium, 211, 225, 241
Darling, W. H. vermillion or vermilion, 208
Davenport, B. F., constant water-bath, 178
milk analysis, 213
De Koninck, L. L., reduction of ferric bromide, 270
De Schulten, A., crystalline cobaltous and ferrous hydrates, 133
De Vries, H., isotonic coefficients of certain salts, 25
De la Harpe, C., and F. Reverdin, detection of carbon monoxide, 108
Dehérain, P. P., exhaustion of soils by cultivation without manures, 293
Dehydrating agents, action of, 267
Delarchanal, M., and C. Vincent, sorbite, 258
Delauney, M., connection of the atomic weights of simple bodies, 208
Delaurier, M., use of coloured gases in photography, 121
Demjanoff, N., pentamethylene and tetramethylene bromides, 133
Dewar, J., and G. D. Liveing, note on the absorption spectra of oxygen and some of its compounds, 75
Dibdin, W. J., "Practical Photometry" (review), 232
Didymium group, 27
Diffusion, note on, 164
Digitaline, crystalline, 258
Dimethyl-aniline, reactions of, 121
Dimethyl-hepta-methylene, formation of, 267
Dimidium, 235
Diphenylfurfuran, 302
Dixon, W. A., formation of coal and carbonaceous minerals, 263
note on diffusion, 164
Divers, E., and T. Haga, oxy-amido sulphonates, 268
Drechsel, E., fission-products of casein, 62
Drown, T. M., influence of silicon on the determination of phosphorus in iron, 20
Dublin University, 137
Dudley, W. L., organic analysis, modification, 74
Durham College of Science, 143
Duter, E., electrolysis of distilled water, 69
Duvillier, E., diethyl-amido-propionic acid, 72
Dyeing, theory of, 73

EASTERFIELD, T. H., handy trough for Hofmann's vapour density apparatus, 250
simple water-bath regulator, 250
Earths, rare, spectroscopic researches on, 27, 39, 51, 63

Eckenroth, H., composition of wine vinegars, 37
Edinburgh University, 145
Eiffel tower, electric conductivity of, 304
Eikonogen, 163
Eissler, M., "Metallurgy of Silver" (review), 22
"Modern Explosives" (review), 314
Electric phenomena, study of, 97
radiation meter, new, 230
spark, photographs of black, 10
Electrical and thermal units, 122
resistance of bismuth, 10
"Electrical Distribution of Heat, Light, and Power" (review), 315
Electrically driving tuning-forks, 230
Electricity, cooking by, 74
influence of on the fixation of nitrogen, 161
Electrification of a steam jet, 303
Electrifications due to contact of gases and liquids, 231, 268
"Electro-Metallurgy" (review), 61
Electrolysis of distilled water, 69, 103
Electrolytic separations, 102, 262
separation of cadmium from zinc, 9
Enamels on tiles, oriental, 319
Engel, R., action of hydrochloric acid, 121
hydrochlorates of the chlorides in general, 121
Enright, J. E., electrifications due to contact of gases and liquids, 231, 268
Equilibrium, study of the conditions, 185
Erbium group, 39
Eschelmann, G., methods of producing chlorine and hydrochloric acid, 221
Evans, R. E., and R. Meldola, note on the oxidation of paradiamides, 56
Ewan, T., and J. B. Cohen, oxidation products of acenaphthene, 59
"Explosives, Modern" (review), 314

FATS, determination of neutral, 109
Feit, W., determination of thallium and mercury, 86
Fermentations, study of pure, 187
Ferric bromide, reduction of, 270
chloride, reaction of, 87
oxide and alumina, determination of, 98
salts, standard solution without titration, 271, 293, 305
sulphate in volumetric analysis, reduction of, 93 159
Ferrier, C., assay of palm and copra oils 258
Ferrocyanides, certain, 62
Fertilising experiments, 246
Fessenden R., rapid filtration, 102
French, W., standard solution of ferric salts without titration, 271, 305
Filemonowicz, J. and B. Pawlewski, solubility of paraffin, 109
Filtering arrangement, 167
Filters, house, and potable waters, 185
Filtration, rapid, 102
Firth College, Sheffield, 145
Flax, constituents of, 280
Fleitmann, M., nature of cobalt and nickel, 8
Flower, W. H., address to British Association, 123
Fluorine, 305
and hydrogen, combination heat of, 97
compounds of vanadium, 210
Fluor-spar in zinc blende, 210
Foerster, O., purification of the colouring matter of litmus, 306
Food, preserved, living germs in, 132
Fox, J. J., and Grace C. and P. F. Frankland. study of pure fermentations, 187
Fragner, M., a novel alkaloid, 73
Frankland, E., storage batteries, 100
water analysis, 281
P. F., Grace C., and J. J. Fox, study of pure fermentations, 187
Frankel, L. K., and E. F. Smith, electrolytic separations, 102, 262
electrolytic separation of cadmium from zinc, 9
Freiburg, laboratory of the University, 62
University, 121
Fresenius, R., and E. Hintz, determination of silicon and iron in cryolite, 85
Friedel, C., and J. M. Crafts, decomposition of the sulpho-conjugated acids, 62
Fuel and its applications, 93
Fucusol, 221
Furfuric compounds, 233
Furfurol, reactions of, 234

GALVANIC combination, origin of the current in, 12
Gas generating apparatus, 98
natural, danger from the use of, 283
Gas-vacuum end-on tubes, re-examination of spectra, 223
Gases, examination of water for dissolved, 109
coloured, use of in photography, 121
Gastine, G., alcoholic fermentation of honey, 197
"Geological Record for 1886" (review), 292
Geometrical optics, note on, 303
Gernez, M., application of the measure of rotatory power, 72
Gerock, E. J., separation of strychnine and brucine, 185
Giraud, H., reactions of dimethylaniline, 121
Gladstone, J. H., and W. H. Perkin, magnetic rotation and the refraction and dispersion of light, 48
Glasgow and West of Scotland Technical College, 145, 160
University, 148
Glass for windows, manufacture of red, 185
Glasses, analysis of, 14, 33, 41
Glucose, new reagent for, 209
Glycerides, stability of the fatty, 42
Glycerin, use in preserving solutions of sulphuretted hydrogen, 235
Gold, action of silicon on, 5
Goppelsroeder, F., "Capillary Analysis" (review), 159
"Appendices to the Investigation on Capillary Analysis" (review), 158
"Chrom-electrochemical Communications" (review), 159
Gore, G., rate of decomposition of chlorine-water by light, 271
Gorgen, A., manganese oxides, 12
Gouy, M., expansion of the spectral rays of the metals, 8
on the Brownian movement, 62
Gray, J. W., "Facts about Railway Rates, &c." (review), 305
Greens, Prussian, rapid analysis of, 73
Gregory, W. G., method of driving tuning-forks electrically, 230
new electric radiation-meter, 230
Grete, A., volumetric determination of phosphoric acid, 310
Griffiths, A. B., salicylic acid, 59
"Manures and their Uses" (review), 244
Grimbert, L., and E. Jungfleisch, analysis of sugars, 306
Gröger, M., determination of neutral fats, 109
Guignet, C. E., combinations of copper oxide with amylaceous bodies, 209
manufacture of red glass for windows, 185
action of ammoniacal copper sulphate. 246
colloid cellulose, 24
Guinochet, C., isomer of carballylic acid, 317
Gustavson, M., pentamethylene and tetramethylene bromides, 133
Guy's Hospital, 174
Gyzander, C. R., filtering arrangement, 167

HADFIELD, R. A., alloys of iron and silicon, 273
Hæmoglobine, spectrum of reduced, 50
Haga, T., and E. Divers, oxyamido-sulphonates, 268
Hager, H., alcohols in ethereal oils, 103
determination of alcohol, 109
Hake, H. W., "Coloured Analytical Tables" (review), 244
Haller, A., camphor and borneol, separation of, 25
isocamphols, 85
Halogens and oxygen, reciprocal displacements between, 251
Haloid compounds, 318
Hambly, F. J., and T. E. Thorpe, phosphoral trifluoride, 254
Hamilton, R., purification of hydrofluoric acid, 252
Hanriot, M., oxidation of triphenylmethane, 121
Hartog, P. J., researches on the sulphites, 84, 97, 185
Hastings, C. W., "Photographic Quarterly" (review), 280
Hautefeuille, P., and J. Margottet, simultaneous synthesis of water and hydrochloric acid, 246
Heat, animal, 282, 293
"Heat, Elementary Treatise" (review), 23
Hermann, L., spectrum of reduced hæmoglobine, 50
Hilger, M., determination of theine, 50
Hintz, E., and R. Fresenius, determination of silicon and iron in cryolite, 85
Hiorns, A. H., "Iron and Steel Manufacture" (review), 292
Hofmann's vapour-density apparatus, handy trough for, 250
Honey, alcoholic fermentation of, 197
dextro-rotatory, 73
Hopkins, F. G., yellow pigment in butterflies, 57
Horse-fat, 277
Hooker, S. C., nitrates in potable water, 110
Hooper, D., tannin in Indian and Ceylon teas, 311
Hughes, J., analysis of concentrated superphosphate, 91
Hundeshagen, F., analytical studies on phosphododekamolybdic acid, 169, 177, 188, 201, 215
Hydrate of thallic oxide, new crystalline, 113
Hydrates, crystalline cobaltous and ferrous, 133
Hydrochlorates of the chlorides, 121
Hydrochloric acid, action of, 121
Hydrogen, absorption of by metals, 25
and fluorine, combination-heat of, 97
spectrum, 208
Hyponitrites, 25

"IMPERIALINE," a novel alkaloid, 73
Indexing chemical literature, report of committee, 224
Industrial reviews and patents, 120
Institute of Chemistry, 109
Institution, Royal, 11, 231, 260, 294, 304
Iodide of amyl, preparation of, 12
Iodine absorption of essential oils, 236, 261, 281, 282
values of oils and fats, 282
Ireland, Royal College of Science for, 146, 161
Iron, annealed, experiments on, 269
and silicon, alloys of, 273
and steel analysis, international standards for, 247
carbon in, determination of, 167
galvanising, 38
in cryolite, determination of, 85
phosphorus in, determination of, 20
"Iron and Steel Manufacture" (review), 292
Irving, A., metamorphism of rocks, 269
"Chemical Studies on the Metamorphism of Rocks" (review), 256
Isocamphols, 85
Isomeric naphthalene derivatives, 287
Istrati, M., chemical composition of the rock-salt of Roumania, 121

JAHACLE, M., origin of the artesian waters of the French Sahara, 209
Jannasch, P., determination of water in silicates, 310
and T. W. Richards, determination of sulphuric acid, 19
Japp, F. R., and A. E. Turner, compounds of phenanthraquinone with metallic salts, 301
and F. Klingemann, constitution of Zinin's lepiden derivatives, 264
Joannis, A., potassium, 317
Johnstone, A., method of detecting metallic silver, 309
new method of detecting tin in minerals. 271
Johnstone, W., milk analysis, 233, 257
Jolles, A., volumetric determination of stannous compounds, 73
Joly, A., ammoniacal compounds of ruthenium, 25
and M. Vézes, certain double nitrates of ruthenium and potassium, 257
Jones, C., reduction of ferric sulphate in volumetric analysis, 93
silicon in pig-iron, 79
Jörgensen, A., "Micro-organisms of Fermentation" (review), 316
Joule, Dr. James Prescott, obituary, 207
Julius, P., theory of dyeing, 73

Jungfleisch, E., and L. Grimbert, analysis of sugars, 306
Jute, detection of, 72

KASAN, Prof. Saytzeff's laboratory, 62, 121
Katayama, K., new reaction for carbon monoxide in blood, 110
Keller, H. F., kobellite from Ouray, Col., 116
Kennepohl, G., determination of ferric oxide and alumina, 98
King's College, 137
Kipping, F. S., and W. H. Perkin, jun., action of dehydrating agents, 267
formation of dimethylheptamethylene, 267
Kipp's apparatus, simple substitute for, 228
Klingemann, F., and F. R. Japp, constitution of Zinin's lepidden devivatives, 264
Knecht, E., and R. Benedikt, "Chemistry of the Coal-Tar Colours" (review), 61
Kobellite from Ouray, Col., 116
Kobert, M., active principle of Panama bark, 120
Koster, A., detection of carbonic acid in potassa-lye, 37
"Kraut," fruit and carrot, 306
Kranzfeld, J., ferrous oxide, 71
Kremel, M., examination of natural oil of bitter almonds, 109
Krüss, G, and M. Althausse, composition and the absorption-spectrum of organic compounds, 240
Kuhara, M., specific volume of camphor and borneol, 114
Künz, G. F., precious stones, 70, 82, 92, 106

LABORATORY instruction, chemical lectures, and classes, 147
Lambert, A., action of borax, 197
Lange, O., determination of nitrogen, 74
Lanoline, identification of, 37
Lascelles, B. P., and R. P. Williams, "Introduction to Chemical Science" (review), 292
"Laundry Management" (review), 231
Laurie, A. P., alloys of lead, tin, zinc, and cadmium, 268
Le Canu, J. A., phenol-disulphonic acid, 185
phenol sulphuric acids, 97
Le Roy, G. A., new method of preparing alkaline nitrites, 24
Lea, C., allotropic forms of silver, 34, 43, 53
Lead chromate, poisoning by cotton dyed with, 74
peroxide, analysis of, 97
Lechartier, G., incineration of vegetable matter, 286
Leroy, C. J. A., object-glasses for the microscope, 305
Letellier, A., researches on the purple of purpura lapillus, 49
"Letts's Diaries for 1890" (review), 305
Lewes, V. B., "Service Chemistry" (review), 220
Light, magnetic rotation and the refraction and dispersion of, 48
on moist oxygen, action of, 255
rate of decomposition of chlorine-water by, 271
"Light, Heat, Power, Electrical Distribution" (review), 315
Lightning photographs, 10
Lime, calcined caustic, 234
separation of small quantities of manganese from a large quantity of, 262
Lindo, D., analysis of glasses, 14, 33, 41
Ling. A., isomeric change in the phenol series, 60
Lion, G., photometry with nitrogen iodide, 248
Litmus, purification of the colouring matter, 306
Liveing, G. D., new photographic developer, 163
and J. Dewar, note on the absorption-spectra of oxygen and some of its compounds, 75
Livermore, W. R., classification of the atomic weights, 164, 178
Liverpool College of Chemistry, 143
Physical Society, 222
University College, 142
Lloyd, Emily J., osmotic pressure, 284, 297
Loiseau, D., fermentation of raffinose, 233
Logwood extract, detection of sugar in, 49
London sewage, 50
University, 135
water supply, 34, 104, 166, 216, 252, 309
Ludwig, M., toxicological search for mercuric chloride, 133
Lundberg case, the, 117, 131
Lunge, J., use of water-gas, 160
Lunt, J., and H. E. Roscoe, estimation of oxygen, 59
Lyte, F. M., danger from the use of natural gas, 283

MACMUNN, C. A., "Outlines of the Clinical Chemistry of Urine" (review), 220
Madan, H. G., "Elementary Treatise on Heat" (review), 23
Maddox, E. E., "Clinical Use of Prisms" (review). 292
Magne, L., manufacture of red glass for windows, 185
Magnesia, precipitation of, 239
Magnesium as a reagent, 187
bronze, 272
Mahla, F., a new salt bordering on potassium ferrocyanide, 185
Maisch, H. C. C., boron, 313
Malbot, H., preparation and purification of amyl iodide, 12
Manna, examination of, 36
Mangin, L., pectic compounds in plants, 221
Manganese, metallic, preparation of, 20
separation of small quantities from a large quantity of lime, 262
oxides, 12
Manures and their uses, 174
farmyard, formenic fermentation of, 305
"Manures and their Uses" (review), 244
Maquenne, M., fucusol, 221
hyponitrites, 25
new relations between the sugars and the furfuric compounds, 233
sugar with an aromatic nucleus, 293
Margottet, J., and P. Hautefeuille, simultaneous synthesis of water and hydrochloric acid, 246
Martinotti, F., determination of nitrogen, 306
Marsh, J. E., researches on the chemistry of the camphoric acids, 307
Massol, M., barium malonates, 37
Mason Science College, Birmingham, 141
Mason, W. P., notes on qualitative analysis, 305
"Notes on Qualitative Analysis" (review), 245
Matter, condition of, near its critical point, 24
Mayer, F., qualitative analysis of the ammonium sulphide precipitate, 272
McCulloch, N., new process for the volumetric estimation of bromine, 259
McIntosh, J. G., vermilion or vermillion, 160
Medical schools, 148
"Medicine, Retrospect of" (review), 61
Meinecke, M. C., analysis of the raw materials and the products of siderurgy, 270
Meldola, R., and R. E. Evans, note on the oxidation of paradiamines, 56
and J. H. Coste, monobenzyl-derivatives of the phenylene diamines, 57
and F. W. Streatfeild, molecular weights of some polymeric compounds, 66
Mendeleeff, D., attempt to app'y to chemistry one of Newton's principles, 1, 15, 30
Mercuric chloride, toxicological search for, 133
Mercury and thallium, determination of, 86
apparatus for measuring and dropping, 98
chlorides, ammoniacal, 317
detection of, 120
haloid salts of, study, 293
Merget, M., detection of mercury, 120
Messinger, J., elementary analysis of organic substances, 73
Metal, crystalline, 174
"Metallurgy of Silver" (review), 22
Metals, absorption of hydrogen by, 25
expansion of the spectral rays of, 8
reduction of the difficultly reducible, 228, 237
Metaphenylene diamine, 293
Michael, A., haloid compounds, 318
and H. Pendleton, alloisomerism in the cinnamic acid series, 210
"Micro-organisms of Fermentation" (review), 316
Microscope, object-glasses for, 305
Milk analysis, 213, 233, 245, 257
cows', utilisation, 197
estimation of fat, 5
rapid estimation of fat in, 214
sodium hydrocarbonate in, 81
Mills, J., and B. North, "Quantitative Analysis" (review), 316
Minerals, carbonaceous, formation of coal and, 263, 275
tin in, new method of detecting, 271
Mines, Royal School of, 138
Moissan, H., anhydrous platinum bifluoride, 291
new researches on fluorine, 305
and M. Berthelot, combination-heat of fluorine and hydrogen, 97
Molecular volumes, 185
weight of substances in solution, 46
weights of certain substances, 189
Monmouthshire University College, 140
Monochlordinitrophenol, derivatives obtained from, 45
Monomethyl-aniline, 11
Morley, H. F., and M. M. P. Muir, "Watts's Dictionary of Chemistry" (review), 256
Muir, M. M. P., and H. F. Morley, "Watts's Dictionary of Chemistry" (review). 256
Mulhouse Industrial Society, 120, 209, 221, 258
Müntz, A., absorption of ammoniacal nitrogen by plants, 246
Mussi, U., separation of cocaine from animal remains, 110

NAHNSEN, R., determination of copper and arsenic in pyrites, 133
Naphthalene derivatives, isomeric, 287
series, isomeric change in, 58
Nelson, F. E., Clarke's soap test, 132
Newton's principles, attempt to apply to chemistry one of, 1, 15, 30
Nickel and cobalt, nature of, 8
separation of, 54
and tungsten alloys, magnetism of, 312
Nickel, E., coloured reaction of carbon compounds, 104
Nitrates, determination, 261
in potable water, detection of, 110
Nitric acid, conditions of action of, 13
magnetic rotation of, 253
oxide, certain reactions of, 121
Nitrites, alkaline preparation of, 24
formation-heats of, 24
Nitrogen, ammoniacal, absorption by plants, 246
atmospheric, experiments on, 97
dioxide, molecular weight of, 25
determination, 74, 306
fixation, 161, 173, 184, 257
iodide, photometry with, 248
Nitrocamphors, thermic researches on isomeric, 62
Nitroso-camphor, oxidising action of, 85
Nitroso-naphthol, application of, 38
Nitrous acid, solidification of, 49
Nodon, A., study of electric phenomena, 97
Noelting, E., "Scientific and Industrial History of Aniline Black" (review), 72
Noerdlinger, H., free fatty acids in oils, 34
North, B., and J. Mills, "Quantitative Analysis" (review), 316

OBITUARY, Dr. John Percy, 11
Dr. James Prescott Joule, 207
Dr. Gustave Quesneville, 269
Odling, W., W. Crookes, and C. M. Tidy, London water supply, 34, 104, 166, 216, 252, 309
Oils, free fatty acids in, 34
essential, detection of adulteration in, 175, 236, 245, 261
iodine absorption of, 236, 261, 281, 282
ethereal, alcohol in, 103
reactions of, 62
palm and copra, assay of, 258
Onslow College of Science, 148
Opificius, L., analysis of lead peroxide, 97
Organic analysis, modification of, 74
Organic compounds, combustion-heat of certain, 161
composition and absorption-spectrum, 240
substances, elementary analysis of, 73

"Organic Chemistry, Text-Book of" (review), 281
Osmotic pressure, 284, 297
Ossipoff, S., combustion-heat of certain organic compounds, 161
Ossipoff, J., supplementary thermic data, 197
Oxamic acid and oxamide, new process for preparing, 245
Oxford University, 136
Oxide, ferrous, 71
of manganese, 12
Oxyamido-sulphonates, 268
Oxygen, absorption-spectra, 75
action of light on moist, 255
and the halogens, reciprocal displacements between, 251
estimation of, 59
Ouray, Col., kobellite from, 116
Owen's College, 135

PACHORUFOFF, M., active principle of Panama bark, 120
Padé, L., sodium hydrocarbonate in milk, 81
Palm and copra oils, assay of, 258
Panama bark, active principle of, 120
Panification, fraudulent, 120
Paradiamines, oxidation of, 56
Paraffin in crude petroleum, 18
solubility of, 109
Parkes, A., thiocamf, 72
Partridge, E. A., paraffin in crude petrodeum, 18
Patein, C., cause of error in detecting albumen, 130
Patrick, G. E., estimation of fat in milk, 5
Pawlewski, B., and J. Filemonowicz, solubility of paraffin, 109
Péchard, E., phosphotungstic acids, 161
Pectic compounds in plants, 221
Pendleton, H., and A. Michael, alloisomerism in the cinnamic acid series, 210
Pendulum experiments, 295, 317
Percy, Dr. John (obituary), 11
Périer, L., solubility of saccharose, 11
Perkin, W. H., action of butyryl chloride, 45
magnetic rotation of nitric acid, &c., in solution, 253
melting-point of some salicylic and anisic compounds, 45
and J. H. Gladstone, magnetic rotation and the refraction and dispersion of light, 48
jun., and F. S. Kipping, action of dehydrating agents, 267
formation of dimethyl heptamethylene, 267
and A. Schloessier, diphenylfurfuran, 302
and J. B. Tingle, acetylcarbinol, 280
Perry, J., behaviour of twisted strips, 231
Petersen, E., fluorine compounds of vanadium, 210
Petit, P., and M. Berthelot, animal heat, &c., 282
formation-heats of the nitrites, 24
thermic researches on isomeric nitrocamphors, 62
Pickering, S. U., law of the freezing-points of solutions, 278
nature of solutions, 46, 68, 253
"Picture-making by Photography" (review), 108
Pig-iron, silicon in, 79
Pipette for measuring juices for polarisation, 55
Pharmaceutical Society, School, 147
Pharmacy, schools of, 147, 148
Phenanthraquinone compounds, 301
Phenol-disulphonic acid, 185
Phenol series, isomeric change in the, 60
Phenol-sulphuric acids, 97
Phenol, variable causticity, 120
Phenyl-thiophene, 269
Philosophy, natural, attempt to apply to chemistry one of Newton's principles, 1, 15, 30
Phipson, T. L., arsenical waters of Court St. Etienne, 67
atomic considerations, 299
Phosphates, action of, 174
Phosphododekamolybdic acid, 169, 177, 188, 201, 215
Phosphonium sulphate, existence of, 246
Phosphoral trifluoride, 254
Phosphoric acid, determination of, 12, 74
volumetric determination of, 310
Phosphoroscope, 64
Phosphorus in iron, determination of, 20
Phosphotungstic acids, 161
Photographic developer, new, 163
"Photographic Quarterly" (review), 280
Photography, use of coloured gases, 121
"Photography, Picture-making" (review), 108
Photometry with nitrogen iodide, 248
"Photometry, Practical" (review), 232
Physical bases for the theory of errors, 230
Society, 10, 230, 268, 303
of Liverpool, 222
Plants, colour, relation to the richness of the soil, 174
Platinates, formation of, 72
Platinoid, thermo-electric position of, 77
Platinum, action of silicon, 5
bifluoride, anhydrous, 291
Plessy, E. M., new process for preparing oxamide and oxamic acid, 245
new reagent for cane-sugar, grape-sugar, and pyrogallic acid, 282
Poison of rabies, principal cause of the attenuation of, 197
Politis, J. E., rapid determination of saccharine matter, 197
Polymeric compounds, molecular weights of some 66
Polytechnic Institute, 148
Portland cement, practical study on, 270
Potash, prussiate of, manufacture, 178
Potassa-lye, detection of carbonic acid in, 37
Potassium and sodium, combination, 317
action of, 121
determination of, 109
permanganate, use of, 121
Preusser, J., determination of tungsten, 37
"Prisms, Clinical Use of" (review), 292
Purple produced by purpura lapillus, 49
Pyrites, determination of sulphur in burnt, 293
Pyrogallic acid, new reagent for, 282

QUALITATIVE analysis, notes on, 305
Queen's College, Belfast, 146
Cork, 146
Galway, 148
Queneville, Dr. Gustave (obituary), 269
Querbracho extract, commercial, 251
two new sugars from, 317

RABIES, poison, principal cause of the attenuation of, 197
Raffinose, 221
fermentation of, 233
"Railway Rates, Facts about" (review), 305
Rammelsberg, C., certain ferrocyanides, 62
Ramsay, W., molecular weight of nitrogen dioxide, 25
Raulin, G., action of phosphates, 174
Readman, J. B., manufacture of prussiate of potash, 178
Red, Turkey, note on, 282
Renard, A., phenyl thiophene, 269
Reverdin, F., and C. De la Harpe, detection of carbon monoxide, 108
Richards, T. W., atomic weight of copper, 110
and P. Jannasch, determination of sulphuric acid, 19
Richardson, A., action of light on moist oxygen, 255
Rideal, S., colorimetric method for the determination of nitrates in potable water, 261
Rigg, E., The British Association, 120
Robinson, H. P., "Picture-making by Photography" (review), 108
Rocks, metamorphism, 269
"Rocks, Metamorphism of" (review), 256
Ræse, B., determination of alcohol, 109
Rogers, A. J., reduction of the difficultly reducible metals, 228, 277
Rommier, A., possibility of changing the bouquet of a wine, 234
Roozeboom, H. W. B., study of the conditions of equilibrium, 185
Roscoe, Sir H. E., and J. Lunt, estimation of oxygen, 59
"Ventilation of Schools" (review), 315
Rotatory power, application of the measure of,
Rothenbach, M., use of water gas, 160
Rousseau, G., barium cobaltites, 49
formation of platinates, 72
Royal Institution, 11, 231, 260, 294, 304
"Royal Society of New South Wales, Journal" (review), 96
Ruthenium, ammoniacal compounds of, 25
and potassium, certain double nitrates of, 257

SACCHARINE in mixtures, detection, 234
matter, rapid determination of, 197
Saccharose, solubility of, 11
Safranine, new reagent for glucose, 209
Saget, G., new process for mordanting with chrome, 209
note on Turkey red, 282
Saint Edme, E., passivity of cobalt, 157
Saint Pierre, O., oxidation of triphenylmethane, 121
Salicylic acid, 59
compounds, melting-point of, 45
Salt, a new, 185
Salts, basic, constitution of, 283
Salts, ferric, standard solution without titration, 271, 293, 305
isotonic coefficients of certain, 25
Saytzeff, Prof., laboratory at Kasan, 62, 121
Schlœsser, A., and W. H. Perkin, jun., diphenylfurfuran, 302
Schlœsing, T., experiments on atmospheric nitrogen, 97
fixation of nitrogen, 173
formenic fermentation of farmyard manure, 305
nitrification of ammonia, 184, 317
Schlœsing, T., jun., air enclosed in the soil, 232
ground air, 258
"Schools, Ventilation of" (review), 315
Schröder, J., detection of antifebrine, 109
Schweissinger, O., detection of sugar in extract of logwood, 49
Science, Normal School, 136
Royal College of, for Ireland, 146, 161
Selenium compounds, synthesis of certain oxygenated, 221
of some, 84
Sewage of London, 50
process, "Amines," 157, 184, 196, 207, 221, 233, 245, 257
Sewage-treatment at Kingston-on-Thames, 12
Seyewitz, A., metaphenylene diamine, 293
Sheffield Mechanics Institution, 148
Sheldon, S., and J. Trowbridge, magnetism of nickel and tungsten alloys, 312
Shilton, A. J., use of glycerin in preserving solutions of sulphuretted hydrogen, 235
Siderurgy, analysis of the raw materials and the products, 270
Silica, estimation of, 227
Silicates, water in, 310
Silver, allotropic forms of, 34, 43, 53
method of detecting metallic, 309
nitrate, reactions of the oils with, 62
volumetric determination of, 90
"Silver, Metallurgy of" (review), 22
Silicon, action of on various metals, 5
&c., quick method of preparing, 158
in cryolite, determination of, 85
influence of in the determination of phosphorus in iron, 20
in pig-iron, 79
on the properties of steel, influence of, 273, 289, 299
Sindall, R. W., bromonaphthalene sulphonic acid, 57
Smith, E. F., and L. K. Frankel, electrolytic separations, 102, 262
electrolytic separation of cadmium from zinc, 9
derivatives obtained from monochlordinitrophenol, 45
Smith, F. J., water-jacketted flexible tube, 187
Smith, the late Charles, 149
Smith, W. J., sulphur compounds of the cruciferæ, 185
"Smithsonian Report" (review), 92
Smyth, C. P., re-examination of spectra of gas-vacuum end-on tubes, 223
Snijers, A., house-filters and potable waters, 185
Snow, H. W., adulteration in essential oils, 248

Soaps and fatty acids in the animal body, action of, 197
Soap test, Clarke's, 132
Society, Chemical, 45, 56, 253, 264, 278, 301
of Mulhouse, Industrial, 120, 209, 221, 258
Physical, 10, 230, 268, 303
of Liverpool, 222
" Society, Royal, of New South Wales, Journal" (review), 96
Sodium hydrocarbonate in milk, 81
nitroprusside, 168
Sohn, C. E., water-bath regulator, 293
Sohncke, L., origin of the current in a galvanic combination, 12
Soil, air enclosed in, 232
Soils, exhaustion by cultivation without manures, 293
Solar spectrum, spectro-photography of the invisible parts of, 184
Solutions, law of the freezing-points of, 278
nature of, 46, 68, 253
Sorbite, 258
Soret, A., electrolysis of copper sulphate, 24
Speak, S. J., constant water-bath, 208
Specific gravity bottle for tropical climates, 236
Spectra, absorption, of oxygen, 75
of gas-vacuum end-on tubes, re-examination of, 223
Spectral rays of the metals, expansion of, 8
Spectroscopic demonstration of traces of blood, 50
researches on the rare earths, 27, 39, 51, 63
Spectro-photography of the invisible parts of the solar spectrum, 184
Spectrum of hydrogen, 208
Spiller, J., experiment in colour-blindness, 247
Stannic chloride, action of water on, 174
Stannous compounds, volumetric determination of, 73
Steam-boilers, analysis of feed-waters, 317
Steam-jet, electrification of, 303
Steel and Iron, analysis, international standards for, 247
behaviour of under mechanical stress, 303
influence of silicon on the properties of, 273, 289, 299
tempering, colours produced during the, 190
"Steel and Iron Manufacture" (review), 292
" Stevens Institute of Technology" (review), 96
Stohmann, F., calorimetric investigations, 121
researches, 210
Stokes, A. W., milk analysis, 233, 245
rapid estimation of fat in milk, 214
Stoklasa, J., determination of phosphoric acid, 12
Stones, precious, 70, 82, 92, 106
Storage batteries, chemistry of, 100
Streatfeild, F. W., and R. Meldola, molecular weights of some polymeric compounds, 66
Strips, twisted, behaviour of, 231
Strychnine and brucine, separation of, 185
Students, hints to, 135
Sugar analysis, 98, 306
new, with an aromatic nucleus, 293
Sugars and the furfuric compounds, new relations between, 233
two new, from querbracho, 317
Sulphate of copper, electrolysis of, 24
phosphonium, 246
Sulphide of ammonium precipitate, qualitative analysis of, 272
of cadmium, 62
Sulphides, separation of, 185
Sulphites, researches on, 84, 97, 185
Sulpho-conjugated acids, decomposition of, 62
Sulphur compounds of the cruciferæ, 185
in burnt pyrites, determination of, 293
molecular magnitude, 25
Sulphuric acid, determination of, 19
improved method of manufacture, 282
Superphosphate, analysis of concentrated, 91
Surgeons, Royal College of, 148
Sworn, S. A., reaction of benzoquinone, 187

TANAKADATE, A., and J. T. Bottomley, thermo-electric position of platinoid, 77
Tanghinine, crystalline, 24
Tannin in Indian and Ceylon teas, 311
physiology of, 74
Tanret, C., two new sugars from querbracho, 317
Tartaric acid, analysis of crude materials containing, 109
Teas, tannin in Indian and Ceylon, 311
Technical College, Bradford, 141
Schools, 147, 148
" Technology, Stevens Institute of" (review), 96
Thallic oxide, new crystalline hydrate of, 113
Thallium and mercury, determination of, 86
Theine, determination of, 50
Thermal and electrical units, 122
Thermic data, supplementary, 197
Thermo-chemistry, application of, 282
Thermo-electric position of platinoid, 77
Thiocamf, 12, 25, 36, 49, 72
Thiophene, phenyl, 269
Thomas, L., and C. Trépied, spectrum of hydrogen, 208
Thomas, M., absorption of hydrogen by metals, 25
Thompson, J. B., pendulum experiments, 295
Thompson, E., simple substitute for Kipp's apparatus, 228
Thompson, S. P., note on geometrical optics, 303
Thorpe, T. E., and F. J. Hambly, phosphoral trifluoride, 254
Tidy, C. M., W. Odling, and W. Crookes, London water supply, 34, 104, 166, 216, 252, 309
Tilden, W. A., "Watts's Manual of Chemistry" (review), 220
Tiles, enamel on oriental, 318
Tingle, J. B., and W. H. Perkin, jun., acetylcarbinol, 280
Tin in minerals, new method of detecting, 271
lead, zinc, &c., alloys, 268
Tomlinson, H., experiments on annealed iron, 269
Trinity College, Dublin, 137
Triphenyl methane, oxidation of, 121
Trowbridge, J., and S. Sheldon, magnetism of nickel and tungsten alloys, 312
Trépied, C., and L. Thomas, spectrum of hydrogen, 208
Tube, water-jacketted, flexible, 187
Tungstates and vanadates, ammonio-cobaltic, 81
Tungsten, determination of, 37, 272
Tuning-forks, method of driving electrically, 230
Turkey-red, note on, 282
Turner, A. E., and F. R. Japp, compounds of phenanthraquinone, 301
Turner, T., colours produced during the tempering of steel, 190
Tuson Fund, 122

UNIVERSITIES and colleges, 135
University College, 138, 240
technical training in chemistry, 68
Dundee, 145
Nottingham, 144
Correspondence College, 148
of Aberdeen, 148
Cambridge, 136
Dublin, 137
Edinburgh, 145
Freiburg, 121
laboratory, 62
Glasgow, 148
London, 135
Oxford, 136
St. Andrews, 146
Victoria, 142
Uranium mine in Cornwall, 234

VANADIUM, fluorine compounds of, 210
Varet, R., ammoniacal mercury chlorides, 317
study of haloid salts of mercury, 293
Vdranzky, L., reactions of furfurol, 234
Vegetable matter, incineration of, 286
Vermicelli, examination of for foreign colours, 85
Vermilion or vermillion, 119, 160, 208
Vernon, H. M., water analysis, 249
Vézes, M., and A. Joly, certain double nitrates of ruthenium and potassium, 257
Viard, G., zinc and cadmium chromites, 72
Victoria Hall, Royal, 148
University, 142
Vignon, L., action of water on stannic chloride, 174, 317
Ville, G., researches on colour of plants, 174
J., dioxyphosphinic acids, 49
M., fertilising experiments, 246
Vincent, C, and M. Delarchenal, sorbite, 258
Volumetric estimation of bromine, 259
Von Aubel, E., electrical resistance of bismuth, 10
Von Klobukow, N., cadmium sulphide, 62
Von Knorre, G., application of nitroso-naphthol, 38
Vosmaer, A., convenient preparation of chromium chloride, 85
Vulpius, G., identification of lanoline, 37

WADSWORTH, G. H., action of aldehyds, 302
Wahl, M., reduction of aluminium, 292
Wales, University College, 139
Waller, E., the Lundberg case, 117, 131
Warden, C. J. H., specific gravity bottle for tropical climates, 236
Warren, H. N., action of silicon on the metals gold, silver, platinum, and mercury, 5
bleaching effects during electrolysis of distilled water, 103
chemistry under high pressure, 42
improved method for the formation of regular crystals, 237
magnesium as a reagent, 187
magnesium bronze, 272
quick method of preparing silicon, &c., 158
T. T. P. B., stability of the fatty glycerides, 42
thiocamf, 36
Water, action of on stannic chloride, 174
analysis, 203, 249, 281
arsenical, of Court St. Etienne, 67
bath, constant, 178, 208
regulator, simple, 250, 269, 293
detection of nitrates in potable, 110
distilled, bleaching effects during electrolysis of, 103
electrolysis of, 69
examination for dissolved gases, 109
gas, use of, 160
in silicates, determination of, 310
jacketted flexible tube, 187
of mines, barium sulphate from, 80
on stannic chloride, action of, 317
artesian, of the French Sahara, origin, 209
of steam boilers, analysis of feed waters, 317
potable, and house filters, 185
supply of London, 34, 104, 166, 216, 252, 309
Watson, G., constitution of basic salts, 283
Watt, A., " Electro-Metallurgy" (review), 61
" Watts' Dictionary of Chemistry" (review), 256
" Watts' Manual of Chemistry" (review), 220
Weights, atomic classification, 164, 178
molecular, of certain substances, 189
of substances in solution, 46
Weyl, T., poisoning by cotton dyed with lead chromate, 74
White, J. T., new alkaloid, 114
vermillion or vermilion, 119
Wiesbaden, chemical laboratory of, 134
Wiley, H. W., molecular weights of certain substances, 189
Williams, R., detection of adulteration in essential oils, 175, 261
R. P., and B. P. Lascelles, " Introduction to Chemical Science" (review), 292
Wilson, C. H. C., behaviour of steel under mechanical stress, 303
J. A., commercial querbracho extract and its detection, 251
iodine values of oils and fats, 282
Wine, possibility of changing the bouquet, 234
vinegar, composition of, 37
Winkler, L. W., examination of water for dissolved gases, 109
Wires, expansion of, 10
Wolff, C. H., spectroscopic demonstration of traces of blood, 50
Wollheim, H., " amines " sewage process, 196, 207, 221, 257
Woukoloff, M., solubility of carbonic acid gas in chloroform, 49

Woussen, M., determination of potassium, 109
Wrampelmeyer, H., apparatus for measuring and dropping mercury, 98
Wright, G. E., thiocamf, 12, 25
Wyss, O., use of water-gas, 160
Wynne, W. P., and H. E. Armstrong, isomeric change in the naphthalene series, 58
YORKSHIRE College, Leeds, 142
Yttrium group, 51
ZEIGLER, A., determination of tungsten, 272
Zenger, C. V., spectro-photography of the invisible parts of the solar spectrum, 184
Zinc and cadmium chromites, 72
chloride, 122
Zinc dextrosate, 57
lead, tin, and cadmium alloys, 268
Zinin's lepiden derivatives, constitution of, 264
Zirconium and its atomic weight, 6, 17, 32

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STUDENTS' NUMBER.

CONTENTS.

ARTICLES:— PAGE
Hints to Students 135
SCHOOLS OF CHEMISTRY:—
University of London—University of Oxford—University of Cambridge—Trinity College, Dublin—Kings College—University College—Normal School of Science and Royal School of Mines—University College of Wales, Aberystwith—University College, Bristol—Royal Agricultural College, Cirencester—Bradford Technical College—The Yorkshire College, Leeds—Mason Science College, Birmingham—University College, Liverpool—Liverpool College of Chemistry—&c..... 135

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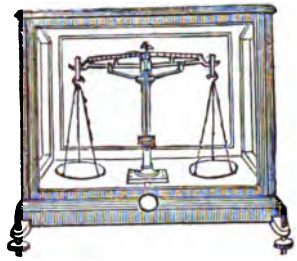

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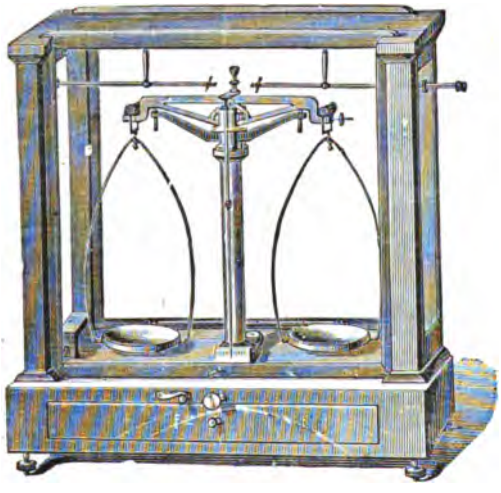

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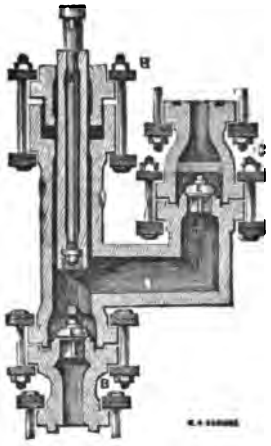

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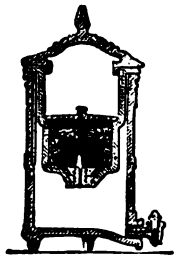

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